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PRECERAMIC POLYMERS TO
HAFNIUM CARBIDE AND HAFNIUM
NITRIDE CERAMIC FIBERS AND MATRICES

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1 This application is a continuation-in-part of an
2 application filed June 3, 1999 under Serial No. 09/325,524
3 and is also a continuation-in-part of the application filed
4 October 6, 2000 which is a continuation-in-part of an
5 application filed June 3, 1999 under Serial No. 09/325,524.

6 BACKGROUND OF THE INVENTION

7 The field of the invention is specific applications of
8 photo curable pre-ceramic polymer chemistry to specific
9 applications.

10 Commercially available high temperature ceramic matrix
11 composites are limited to carbon fiber/carbon matrix, carbon
12 fiber/SiC matrix, SiC fiber/SiC matrix, and more recently,
13 carbon or SiC fiber in a silicon nitride/carbide matrix.
14 The upper use temperature is limited to below 1600 degrees

1 centigrade at best for all but carbon/carbon, which is
2 highly susceptible to oxidation above 400 degrees
3 centigrade. Carbon/carbon can be utilized at ultra high
4 temperatures (above 2000 degrees centigrade) but only in a
5 non-oxidizing environment. The limitations of carbon/
6 carbon, the only truly ultra high temperature CMC system
7 currently available, and the need for new ceramic materials
8 was summarized by Opeka quite recently: "Ultrahigh
9 temperature applications such as combustion chamber liners,
10 rocket thrusters, thermal protection systems for carbon-
11 carbon composites, and leading edges of the spacecraft
12 require materials, which are protective and oxidation
13 resistant at temperatures higher than 2000 degrees
14 centigrade. Refractory ceramics such as hafnium diboride
15 (HfB_2), hafnium carbide (HfC) and hafnium nitride (HfN) are
16 candidate materials because of their high melting points,
17 low coefficient of thermal expansion, high erosion and
18 oxidation resistance." Arvind Agarwal, Tim McKeechnie,

1 Stuart Starett and Mark M. Opeka, Proceedings for the
2 symposium of Elevated Temperature Coatings IV. 2001 TMS
3 Annual Meeting New Orleans, Louisiana, pp. 301-315.

4 U. S. Patent No. 4,864,186 teaches an electric light
5 filament that includes a single crystal whisker that
6 consists essentially of silicon carbide (SiC), preferably
7 beta silicon carbide, doped with a sufficient amount of
8 nitrogen to render the whisker sufficiently electrically
9 conductive to be useful as a light bulb filament at
10 household voltages. Filaments made of such materials
11 are characterized by high strength, durability, and
12 resilience, and have higher electrical emissivities than
13 tungsten filaments.

14 U. S. Patent No. 6,042,883 teaches a method for making
15 surface a precursor polymer that decomposes to a
16 substantially pure product selected from the group
17 consisting of a refractory metal carbide and a refractory
18 metal boride, and exposing the precursor polymer to

1 conditions effective to decompose the precursor polymer to
2 said substantially pure product.

3 U. S. Patent No. 5,750,450 teaches high temperature
4 ablation resistant ceramic composites that have been made.
5 These ceramics are composites of zirconium diboride and
6 zirconium carbide with silicon carbide, hafnium diboride and
7 hafnium carbide with silicon carbide and ceramic composites
8 that contain mixed diborides and/or carbides of zirconium
9 and hafnium, along with silicon carbide.

10 U. S. Patent No. 5,332,701 teaches ceramic compositions
11 that can be formed by the pyrolysis of a particulate metal.

12 The particulate metal forms a component of the ceramic and
13 another metal that forms another component of the ceramic.

14 The rationale for producing a nanocomposite, rather than
15 phase pure HfC or HfN, is that the presence of both carbon
16 and nitrogen hinder the formation of long-range order and
17 allow the HfCN nanocomposite to be processed at high
18 temperature in an amorphous "glassy" state prior to

1 crystallization. This retention of the "glassy" state to
2 high temperatures (>1400 degrees centigrade) in the silicon
3 nitride/carbide (SiNC) system has been seen. In the case of
4 HfCN, the temperature of crystallization should be even
5 higher due to the fact that hafnium is tetravalent in HfC
6 and trivalent in HfN. In addition, the melting points of
7 HfC and HfN are significantly higher than that of silicon
8 carbide and silicon nitride.

9 U. S. Patent No. 4,800,211 teaches 3-Hydroxybenzo[b]
10 thiophene-2-carboxamide derivatives which have been prepared
11 by treating a substituted 2-halobenzoate with a
12 thioacetamide, treating a substituted thiosalicylate with an
13 appropriately substituted haloacetamide and further
14 synthetic modification of compounds prepared above. These
15 compounds have been found to be effective inhibitors of both
16 cyclooxygenase and lipoxygenase and thereby useful in the
17 treatment of pain, fever, inflammation, arthritic
18 conditions, asthma, allergic disorders, skin diseases,

1 cardiovascular disorders, psoriasis, inflammatory bowel
2 disease, glaucoma or other prostaglandins and/or leukotriene
3 mediated diseases.

4 U. S. Patent No. 4,588,832 teaches a novel and
5 economical route for the synthetic preparation of a 1-
6 alkynyl trihydrocarbyl silane compound. The method includes
7 the steps of reacting metallic sodium with a hydrocarbyl-
8 substituted acetylene or allene compound to form a
9 substituted sodium acetylide and reacting the acetylide with
10 a trihydrocarbyl monohalogenosilane in the reaction mixture
11 which is admixed with a polar organic solvent such as
12 dimethylformamide.

13 U. S. Patent No. 4,806,612 teaches pre-ceramic
14 actylenic polysilanes which contain $--(CH_2)_w C.tbd.CR'$
15 groups attached to silicon where w is an integer from 0 to 3
16 and where R' is hydrogen, an alkyl radical containing 1 to 6
17 carbon atoms, a phenyl radical, or an $--SiR''(3)$ radical
18 wherein R'' is an alkyl radical containing 1 to 4 carbon

1 atoms. The acetylenic polysilanes are prepared by reacting
2 chlorine-or bromine-containing polysilanes with either a
3 Grignard reagent of general formula $R'C.tbd.C(CH_2)(w) MgX'$
4 where w is an integer from 0 to 3 and X' is chlorine,
5 bromine, or iodine or an organolithium compound of general
6 formula $R'C.tbd.C(CH_2)(w) Li$ where w is an integer from 0
7 to 3. The acetylenic polysilanes can be converted to
8 ceramic materials by pyrolysis at elevated temperatures
9 under an inert atmosphere.

10 U. S. Patent No. 4,505,726 teaches an exhaust gas
11 cleaning device provided with a filter member which collects
12 carbon particulates in exhaust gases discharged from a
13 diesel engine and an electric heater for burning off the
14 particulates collected by the filter member. The filter
15 member is composed of a large number of intersecting porous
16 walls that define a large number of inlet gas passages and
17 outlet gas passages that are adjacent to each other. The
18 electric heater is composed of at least one film-shaped

1 heating resistor that is directly formed on the upstream end
2 surface of the filter member so as to be integral therewith.
3 When the amount of carbon particulates collected by the
4 filter member reaches a predetermined level, electric
5 current is supplied to the electric heater. The carbon
6 particulates adhered to the upstream end surface of the
7 filter member are ignited and burnt off. Then, the
8 combustion of carbon particulates spreads to the other
9 carbon particulates collected in the other portion of the
10 filter member.

11 U. S. Patent No. 5,843,304 teaches a materials-
12 treatment system which includes filtration and treatment of
13 solid and liquid components of a material, such as a waste
14 material. A filter or substrate assembly is provided which
15 allows liquids to pass therethrough, while retaining solids.
16 The solids are then incinerated utilizing microwave energy,
17 and the liquids can be treated after passing through the
18 filter element, for example, utilizing a treatment liquid

1 such as an oxidant liquid. The filter assembly can also
2 include an exhaust filter that removes solids or particulate
3 matter from exhaust gasses, with the retained solids/
4 particulates incinerated utilizing microwave energy.

5 U. S. Patent No. 5,074,112 teaches a filter assembly
6 for an internal combustion engine which includes, in
7 combination, a housing defining an exhaust gas passage
8 having an inlet end and an outlet end and a cavity
9 intermediate the inlet and outlet ends thereof and in serial
10 fluid communication therewith, the cavity defining an
11 electro-magnetically resonant coaxial line wave-guide, a
12 filter disposed within the cavity for removing particulate
13 products of combustion from exhaust gases passing through
14 the cavity, and a mechanism for producing axis-symmetrically
15 distributed, standing electromagnetic waves within the
16 cavity whereby to couple electromagnetic energy in the waves
17 into lossy material in the cavity to produce heat for
18 incinerating the particulate products of combustion

1 accumulated on the filter.

2 U. S. Patent No. 4,934,141 teaches a device for
3 microwave elimination of particles contained in the exhaust
4 gases of diesel engines in which a microwave source and a
5 conductor of the electromagnetic field generated by the
6 source is joined with a resonator mounted on an element of
7 the pipe for the exhaust gases which contains an insert,
8 characterized by the fact that the insert consists of a
9 filter whose upstream and downstream ends are offset toward
10 the inside of the cavity defined by the resonator and
11 delimit two chambers in which conductors of the electro-
12 magnetic field come out, respectively.

13 U. S. Patent No. 4,825,651 teaches a device and method
14 for separating soot or other impurities from the exhaust
15 gases of an internal-combustion engine, particularly a
16 diesel internal-combustion engine, comprises a microwave
17 source that is coupled to the intermediate section of the
18 exhaust pipe that is constructed for the development of an

1 electromagnetic field, an effective burning of the soot with
2 a low flow resistance, the intermediate section being
3 developed as a cavity resonator and at its exhaust gas inlet
4 and exhaust gas outlet, is equipped with a metal grid, and
5 an insert made of a dielectric material in the cavity
6 resonator concentrates the exhaust gas flow in the area of
7 high energy density of the electromagnetic field.

8 U. S. Patent No. 4,477,771 teaches conductive
9 particulates in the form of soot which are collected from
10 diesel engine exhaust gases on a porous wall monolithic
11 ceramic filter in such a way that the soot is somewhat
12 uniformly distributed throughout the filter. The filter is
13 housed in a chamber having a property of a microwave
14 resonant cavity and the cavity is excited with microwave
15 energy. As the particulates are collected the cavity
16 appears to the microwaves to have an increasing dielectric
17 constant even though the matter being accumulated is
18 conductive rather than dielectric so that as collected on

1 the porous filter it has the property of an artificial
2 dielectric. The response of the cavity to the microwave
3 energy is monitored to sense the effect of the dielectric
4 constant of the material within the cavity to provide a
5 measure of the soot content in the filter.

6 U. S. Patent No. 5,902,514 teaches a material for
7 microwave band devices that are used by the general people
8 and in industrial electronic apparatuses. Particularly, a
9 magnetic ceramic composition for use in microwave devices, a
10 magnetic ceramics for use in microwave devices and a
11 preparation method therefore are disclosed, in which the
12 saturation magnetization can be easily controlled, and a low
13 ferri-magnetic resonance half line width and an acceptable
14 curie temperature are ensured. The magnetic ceramic
15 composition for microwave devices includes yttrium oxide
16 (Y(2) O(3)), iron oxide (Fe(2) O(3)), tin oxide (SnO(2)),
17 aluminum oxide (Al(2) O(3)) and a calcium supply source.
18 The magnetic ceramics for the microwave devices are

1 manufactured by carrying out a forming and a sintering after
2 mixing: yttrium oxide, iron oxide, tin oxide, aluminum oxide
3 and calcium carbonate (or calcium oxide) based on a formula
4 shown below. It has a saturation magnetization of 100-1,800
5 G at the normal temperature, a temperature coefficient for
6 the saturation magnetization of 0.2%/ degree Centigrade, and
7 a ferri-magnetic resonance half line width of less than 60
8 Oe, $Y(3-x) Ca(x/2) Sn(x/2) Fe(5-y) Al(y) O(12)$ where
9 $0.1 \leq x \leq 1$, and $0.1 \leq y \leq 1.5$.

10 U. S. Patent No. 5,843,860 teaches a ceramic
11 composition for high-frequency dielectrics which includes
12 the main ingredients of $ZrO(2)$, $SnO(2)$ and $TiO(2)$ and a
13 subsidiary ingredient of $(Mn(NO(3))(2).4H(2) O)$. A
14 homogeneous ceramic composition can be prepared by a process
15 which includes the steps of adding $ZrO(2)$, $SnO(2)$ and $TiO(2)$
16 by the molar ratio to satisfy $(ZrO(2))(1-x) (SnO(2))(x)$
17 $(TiO(2))(1+y)$ (wherein, 0.1M degrees centigrade or above and
18 adding 1% or less of $Mn(NO(3))(2).4H(2) O$ by weight of MnO

1 to the mixture. The ceramic composition has a high
2 dielectric constant of 40 or more, a quality factor of 7000
3 or more, and a temperature coefficient of resonance
4 frequency below 10. Accordingly, it can be used for an
5 integrated circuit at microwave as well as at high
6 frequency, or for dielectric resonators.

7 U. S. Patent No. 5,808,282 teaches a microwave
8 susceptor bed which is useful for sintering ceramics,
9 ceramic composites and metal powders. The microwave
10 susceptor bed contains granules of a major amount of a
11 microwave susceptor material, and a minor amount of a
12 refractory parting agent, either dispersed in the susceptor
13 material, or as a coating on the susceptor material.
14 Alumina is the preferred susceptor material. Carbon is the
15 most preferred parting agent. A sintering process uses the
16 bed to produce novel silicon nitride products.

17 U. S. Patent No. 5,446,270 teaches a composition that
18 includes susceptors having the capability of absorbing

1 microwave energy and a matrix. The susceptors includes a
2 particulate substrate substantially non-reflective of
3 microwave energy and a coating capable of absorbing
4 microwave energy. The matrix is substantially non-
5 reflective of microwave energy. Susceptors are typically
6 particles having a thin-film coating thereon. The matrix
7 typically includes polymeric or ceramic materials that are
8 stable at temperatures conventionally used in microwave
9 cooking. The composition allows reuse of the susceptors,
10 eliminates decline in heating rate, eliminates arcing,
11 allows the heating rate to be controlled, allows overheating
12 to be controlled, and allows formation of microwave heatable
13 composite materials having very low metal content.

14 U. S. Patent No. 5,365,042 teaches a heat treatment
15 installation for parts made of a composite material which
16 has a ceramic matrix and which includes a treatment
17 enclosure. The treatment enclosure is connected to a
18 microwave generator by a wave-guide and which includes a

1 press for hot pressing a part to be treated in the enclosure
2 and a gas source for introducing a protective gas into the
3 enclosure.

4 U. S. Patent No. 5,126,529 teaches a method for forming
5 a three-dimensional object by thermal spraying which
6 utilizes a plurality of masks positioned and removed over a
7 work surface in accordance with a predetermined sequence.
8 The masks correspond to cross sections normal to a
9 centerline through the work-piece. One set of masks defines
10 all cross sections through the work-piece. A second set of
11 masks contains at least one mask. The mask corresponds to
12 each mask of the first set. Masks from each set are
13 alternatively placed above a work surface and sprayed with
14 either a deposition material from which the work-piece will
15 be made or a complementary material. In this manner, layers
16 of material form a block of deposition material and
17 complementary material. The complementary material serves
18 as a support structure during forming and is removed.

1 Preferably, the complementary material has a lower melting
2 temperature than the deposition material and is removed by
3 heating the block. Alternatively, one could mask only for
4 the deposition material and remove complementary material
5 overlying the deposition material after each spraying of
6 complementary material.

7 U. S. Patent No. 4,199,387 teaches an air filter unit
8 of the pleated media, high efficiency type. The media pleat
9 edges are sealed to the supporting frame to prevent bypass
10 of air with a ceramic adhesive and fibrous ceramic mat which
11 allows the unit to be exposed to high temperatures (e.g., up
12 to 2000 deg. F.) without danger of seal breakdown. While in
13 the form of a slurry, the adhesive is applied, for example,
14 with a trowel to the zig-zag pleated edges of the media
15 which, together with corrugated spacers, forms the filter
16 core. The latter is then surrounded on four sides by the
17 compressible mat of fibrous ceramic material and inserted in
18 a box-like support frame with the slurry filling the space

1 between the pleated edges of the media and the fibrous mat.
2 The filter core and the surrounding mat are assembled with
3 the support frame while the slurry is still wet whereby,
4 upon hardening, the resulting layers of ceramic cement
5 provide a complete, heat-resistant seal while avoiding
6 cracking in normal handling due to the resilience of the
7 compressed fibrous mat which maintains an airtight seal
8 between hardened ceramic and support frame.

9 U. S. Patent No. 6,063,150 teaches a self-cleaning
10 particle filter for Diesel engines which includes a filter
11 housing, control circuitry, a removable filter sandwich and
12 independent power source. The removable filter sandwich
13 includes a number of sintered metal strips sewn and
14 positioned between two sheets of inorganic material to
15 provide a filter sandwich. Current is delivered to the
16 metal filter strips to efficiently burn off carbon, lube oil
17 and unburned fuel particulates that have been filtered from
18 exhaust gas. The filter sandwich is formed into a

1 cylindrical configuration and mounted onto a perforated
2 metal carrier tube for receiving and filtering exhaust gas.

3 U. S. Patent No. 6,101,793 teaches an exhaust gas
4 filter having a ceramic filter body is configured such that
5 a specific heat h (cal/g deg. C.) of ceramic powder
6 constituting the body, and a bulk specific gravity d
7 (g/cm(³)) of the filter, satisfy the relation 0.12
8 (cal/cm(³) deg. C.) $\leq h \cdot d \leq 0.19$ (cal/cm(³) deg. C.). The
9 ceramic filter body includes a plurality of cells that
10 extend axially to open at opposite ends of the body. One of
11 the opposite axial ends of each of the cells is closed by a
12 filler in such a manner that the closed ends of the cells
13 and the open ends of the cells are arranged in an
14 alternating configuration. The filter traps particulates in
15 the exhaust gas, and the trapped particulates are removed by
16 regeneration combustion of the filter. The filter exhibits
17 excellent durability, thus preventing the formation of
18 cracks in the surface and interior of the filter. When the

1 filter is mounted on a diesel engine, the diesel engine
2 advantageously does not discharge black smoke.

3 U. S. Patent No. 5,756,412 teaches a dielectric ceramic
4 composition for microwave applications which consists
5 essentially of the compound having a formula $B'B(2)O(6)$,
6 wherein B' is at least one metal selected from the group of
7 Mg, Ca, Co, Mn, Ni and Zn, and wherein B" is one of Nb or Ta,
8 and additionally includes at least one compound selected
9 from the group of CuO, $V(2)O(5)$, $La(2)O(3)$, $Sb(2)O(5)$,
10 $WO(3)$, $MnCO(3)$, MgO, $SrCO(3)$, ZnO, and $Bi(2)O(3)$ as an
11 additive, wherein the amount of the additive is 0.05% to
12 2.0% by weight of the total weight of the composition.

13 The synthesis of polycarbosilane from the pyrolytic
14 condensation reaction of polydimethylsilane obtained from
15 the reaction of dichlorodimethylsilane with an alkali metal,
16 such as sodium. In the latter approach, polydimethylsilane
17 can be prepared by Würtz type coupling of dichlorodimethyl-
18 silane with sodium in toluene. The direct pyrolysis of

1 polydimethylsilane, a viscous thermoplastic resin, at high
2 temperature gives SiC in a ceramic yield of about 30%-40%.
3 By thermally cross-linking the polydimethylsilane into an
4 infusible rigid thermoset polymer, which is insoluble in any
5 common solvents, the subsequent pyrolysis yield is on the
6 order of 88%-93%. This thermolysis was accomplished by
7 refluxing the polydimethyl-silane to in excess of 350°C.

8 Numerous pre-ceramic polymers with improved yields of
9 the ceramic have been described in U. S. Patent No.
10 5,138,080, U. S. Patent No. 5,091,271, U. S. Patent No.
11 5,051,215 and U. S. Patent No. 5,707,471. The fundamental
12 chemistry contained in these embodiments is specific to the
13 process employed and mainly leaves the pre-ceramic polymer
14 in a thermoplastic state. These pre-ceramic polymers which
15 catalytic or photo-induced cross-linking do not satisfy the
16 high ceramic yield, purity and fluidity in combination with
17 low temperature cross-linking ability necessary for

1 producing large densified ceramic structures in a single
2 step continuous process.

3 U. S. Patent No. 5,138,080 teaches a novel polysila-
4 methylenosilane polymers which has polysilane-poly-
5 carbosilane skeleton which can be prepared in one-step
6 reaction from mixtures of chlorosilaalkanes and organochloro
7 silanes with alkali metals in one of appropriate solvents or
8 in combination of solvents thereof. Such polysilamethyleno
9 silane polymers are soluble and thermoplastic and can be
10 pyrolyzed to obtain improved yields of silicon carbide at
11 atmospheric pressure.

12 U. S. Patent No. 5,091,271 teaches a shaped silicon
13 carbide-based ceramic article that has a mechanical strength
14 and that is produced at a high efficiency by a process
15 including the step of forming an organic silicone polymer,
16 for example, polycarbosilastyrene copolymer, into a
17 predetermined shape, for example, a filament or film; doping
18 the shaped polymer with a doping material consisting of at

1 least one type of halogen, for example, bromine or iodine,
2 in an amount of 0.01% to 150% based on the weight of the
3 shaped polymer, to render the shaped polymer infusible; and
4 pyrolyzing the infusible shaped polymer into a shaped SiC-
5 based ceramic article at a temperature of 800° C to 1400° C
6 in an inert gas atmosphere, optionally the halogen-doped
7 shaped polymer being treated with a basic material, for
8 example, ammonia, before the pyrolyzing step, to make the
9 filament uniformly infusible.

10 U. S. Patent No. 5,300,605 teaches poly(I-hydro-1-R-1-
11 silapent-3-ene) homopolymers and copolymers which contain
12 silane segments with reactive silicon-hydride bonds and
13 contain hydrocarbon segments with cis and trans carbon-
14 carbon double bonds.

15 U. S. Patent No. 5,171,810 teaches random or block
16 copolymers with (I-hydro-I-R-I-sila-cis-pent-3-ene), poly(I-
17 hydro-1-R-3,4 benzo-1-sila pent-3-ene) and disubstituted I-
18 silapent-3-ene repeating units of the general formula ##STRI##

1 where R is hydrogen, an alkyl radical containing from one to
2 four carbon atoms or phenyl, R. sup. 1 is hydrogen, an alkyl
3 radical containing from one to four carbon atoms, phenyl or a
4 halogen and R.sup.2 is hydrogen, or R. sup.1 and R. sup. 2 are
5 combined to form a phenyl ring, are prepared by the anionic
6 ring opening polymerization of silacyclopent-3-enes or 2-
7 silaindane with an organometallic base and cation coordinating
8 ligand catalyst system or a metathesis ring opening catalyst
9 system.

10 U. S. Patent No. 5,169,916 Poly(I -hydro- I -R- I -
11 sila-cis-pent-3-ene) and poly(I -hydro- I -R-3,4 benzo-1-
12 sila pent-3-ene) polymers which has repeating units of the
13 general formula polycarbosilane containing at least two
14 tbd.SiH groups per molecule via intimately contacting such
15 fusible polycarbosilane with an effective hardening amount
16 of the vapors of sulfur.

17 U. S. Patent No. 5,064,915 teaches insoluble poly-
18 carbosilanes, readily pyrolyzed into silicon carbide ceramic

1 materials such as SiC fibers, are produced by hardening a
2 fusible polycarbosilane containing at least two tbd. SiH
3 groups per molecule via intimately contacting such fusible
4 polycarbosilane with an effective hardening amount of the
5 vapors of sulfur.

6 U. S. Patent No. 5,049,529 teaches carbon nitride ceramic
7 materials which are produced by hardening a fusible
8 polycarbosilane containing at least two tbd.SiH groups per
9 molecule by intimately contacting such fusible polycarbosilane
10 with an effective hardening amount of the vapors of sulfur,
11 next, heat treating the infusible polycarbosilane which
12 results under an ammonia atmosphere to such extent as to
13 introduce nitrogen into the infusible polycarbosilane without
14 completely removing the carbon therefrom and then heat
15 treating the nitrogenated polycarbosilane in a vacuum or in an
16 inert atmosphere to such extent as to essentially completely
17 convert it into a ceramic silicon carbon nitride.

1 U. S. Patent No. 5,051,215 teaches a rapid method of
2 infusibilizing pre-ceramic polymers that includes treatment of
3 the polymers with gaseous nitrogen dioxide. The infusibilized
4 polymers may be pyrolyzed to temperatures in excess of about
5 800°C to yield ceramic materials with low oxygen content and,
6 thus, good thermal stability. The methods are especially
7 useful for the production of ceramic fibers and, more
8 specifically, to the on-line production of ceramic fibers.

9 U. S. Patent No. 5,028,571 teaches silicon nitride
10 ceramic materials which are produced by hardening a fusible
11 polycarbosilane containing at least two dbd.SiH groups per
12 molecule by intimately contacting such fusible polycarbo-
13 silane with an effective hardening amount of the vapors of
14 sulfur and then pyrolyzing the infusible polycarbosilane
15 which results under an ammonia atmosphere.

16 U. S. Patent No. 4,847,027 teaches a method for the
17 preparation of ceramic materials or articles by the pyrolysis
18 of pre-ceramic polymers wherein the pre-ceramic polymers are

1 rendered infusible prior to pyrolysis by exposure to gaseous
2 nitric oxide. Ceramic materials with low oxygen content,
3 excellent physical properties, and good thermal stability can
4 be obtained by the practice of this process. This method is
5 especially suited for the preparation of ceramic fibers.

6 U. S. Patent No. 5,714,025 teaches a method for preparing
7 a ceramic-forming pre-preg tape that includes the steps of
8 dispersing in water a ceramic-forming powder and a fiber,
9 flocculating the dispersion by adding a cationic wet strength
10 resin and an anionic polymer, dewatering the flocculated
11 dispersion to form a sheet, wet pressing and drying the sheet,
12 and coating or impregnating the sheet with an adhesive
13 selected from the group consisting of a polymeric ceramic
14 precursor, and a dispersion of an organic binder and the
15 materials used to form the sheet. The tape can be used to
16 form laminates, which are fired to consolidate the tapes to a
17 ceramic.

1 U. S. Patent No. 5,707,471 teaches a method for preparing
2 fiber reinforced ceramic matrix composites which includes the
3 steps of coating refractory fibers, forming the coated fibers
4 into the desired curing the coated fibers to form a pre-preg,
5 heating the pre-preg to form a composite and heating the
6 composite in an oxidizing shape, environment to form an in
7 situ sealant oxide coating on the composite. The refractory
8 fibers have an interfacial coating thereon with a curable pre-
9 ceramic polymer that has a char containing greater than about
10 50% sealant oxide atoms. The resultant composites have good
11 oxidation resistance at high temperature as well as good
12 strength and toughness.

13 U. S. Patent No. 5,512,351 teaches a new pre-preg
14 material which has good tack drape properties and feasible
15 out-time. The pre-preg material is prepared by impregnating
16 inorganic fibers with a composition which includes a fine
17 powder of a metal oxide or oxides having an average particle
18 diameter of not larger than one micrometer, a soluble

1 siloxane polymer having double chain structure, a
2 trifunctional silane compound having at least one
3 ethylenically unsaturated double bond in the molecule
4 thereof, a organic peroxide and a radically polymerizable
5 monomer having at least two ethylenically unsaturated double
6 bonds and heating the impregnated fibers.

7 U. S. Patent No. 4,835,238 teaches a reaction of 1,1-
8 dichloro-silacyclobutanes with nitrogen-containing
9 difunctional nucleophiles which gives polysilacyclobuta-
10 silazanes which can be crosslinked and also converted to
11 ceramic materials.

12 Numerous processing mechanics with various direct
13 applications have been described, for example, in the U. S.
14 Patent No. 5,820,483, U. S. Patent No. 5,626,707, U. S.
15 Patent No. 5,732,743 and U. S. Patent No. 5,698,055. The
16 process mechanics are for a single product process and do
17 not permit continuous curing and pyrolysis in a single step
18 to produce highly dense thick ceramic components.

1 U. S. Patent No. 5,820,483 teaches methods for
2 manufacturing a shaft for a golf club. A plug is detachably
3 affixed to a distal end of a mandrel. A plurality of plies
4 of pre-preg composite sheet are wrapped around the mandrel
5 and plug and, thereafter, heated causing the resin
6 comprising the various plies to be cured. The mandrel is
7 then removed from the formed shaft, leaving the plug as an
8 integral part of the distal tip of the shaft.

9 U. S. Patent No. 5,626,707 teaches an apparatus which
10 produces a composite tubular article. The apparatus includes
11 a frame, a drive mechanism for rotating a mandrel, at least
12 two spindles mounted to the frame, a tensioner and a belt
13 extending between the first and second spindles. The
14 apparatus may be used to roll pre-preg strips or similar
15 sheets of composite materials around the mandrel. The belt
16 travels over the spindles, and the spindles guide the belt
17 through changes in its direction of travel. The mandrel is
18 mounted in the drive mechanism in contact with the belt, which

1 changes its direction of travel around the mandrel. The lower
2 surface of the belt bears against upper portions of the
3 spindles, and the mandrel contacts the upper surface of the
4 belt. As the drive mechanism rotates the mandrel, pre-preg
5 sheets are fed between the mandrel and the belt and are
6 thereby wrapped around the mandrel. The belt presses the pre-
7 preg sheets against the mandrel. The wrapped mandrel may then
8 be removed from the apparatus and cured in any suitable manner
9 known in the art to produce the a composite tubular article.

10 U. S. Patent No. 5,732,743 teaches a method for joining
11 and repairing pipes includes the step of utilizing photo-
12 curable resins in the form of a fabric patch to for quickly
13 repairing or sealing pipes. A photo-curable flexible pre-preg
14 fabric is wrapped over the entire area of the pipe to be
15 joined or repaired. The pre-preg fabric contains multiple
16 layers of varying widths and lengths. The pre-preg fabric is
17 then exposed to photo-radiation which cures and seals the
18 pipe.

1 U. S. Patent No. 5,698,055 teaches a method for making a
2 reinforced tubular laminate. A dry braided fiber sleeve is
3 placed between a mandrel and spiral tape wrap either over,
4 under, or layered with a pre-preg material. During the
5 initial stages of the curing process, while the temperature is
6 rising, the resin in the pre-preg material flows and wets out
7 the dry braid. When the final cure takes place, the braid
8 becomes an integral part of the finished laminate. The choice
9 of fiber materials and braid angle permits various tubular
10 laminate strengths. The selection of fiber colors and
11 patterns permit a wide variety of tubular laminate aesthetic
12 characteristics.

13 U. S. Patent No. 5,632,834 teaches sandwich structures
14 which are made of fiber-reinforced ceramics. The base
15 substance of the ceramic matrix consists of a Si-organic
16 polymer and a ceramic or metallic powder. A cross-linking of
17 the Si-organic polymer takes place under increased pressure
18 and at an increased temperature. After the joining of the

1 facings and the honeycomb core, the sandwich structure is
2 pyrolysed to form a ceramic material

3 U. S. Patent No. 5,641,817 teaches organometallic ceramic
4 precursor binders which are used to fabricate shaped bodies by
5 different techniques. Exemplary shape making techniques which
6 utilize hardenable, liquid, organometallic, ceramic precursor
7 binders include the fabrication of negatives of parts to be
8 made (e.g., sand molds and sand cores for metalcasting, etc.),
9 as well as utilizing ceramic precursor binders to make shapes
10 directly (e.g., brake shoes, brake pads, clutch parts,
11 grinding wheels, polymer concrete, refractory patches and
12 liners, etc.). A thermosettable, liquid ceramic precursors
13 provides suitable-strength sand molds and sand cores at very
14 low binder levels and, upon exposure to molten metal casting
15 exhibit low emissions toxicity as a result of their high char
16 yields of ceramic upon exposure to heat. The process involves
17 the fabrication of preforms used in the formation of composite
18 articles. Production costs, and relatively poor physical

1 properties prohibits their inherently large cost of
2 capitalization, high wide use.

3 U. S. Patent No. 4,631,179 teaches this ring-opening-
4 polymerization reactions method to obtain a linear polymer
5 of the formula $[\text{SiH}_{.2} \text{CH}_{.2}]_{.n}$. This polymer
6 exhibit ceramics yields up to 85% on pyrolysis. The
7 starting material for the ring-opening-polymerization
8 reaction was the cyclic compound $[\text{SiH}_{.2} \text{CH}_{.2}]_{.2}$,
9 which is difficult and costly to obtain in pure
10 form by either of the procedures that have been reported.

11 U. S. Patent No. 5,888,641 teaches an exhaust manifold
12 for an engine which is made of all fiber reinforced ceramic
13 matrix composite material so as to be light weight and high
14 temperature resistant. A method of making the exhaust
15 manifold includes the steps of forming a liner of a cast
16 monolithic ceramic material containing pores, filling the
17 pores of the cast monolithic ceramic material with a pre-
18 ceramic polymer resin, coating reinforcing fibers with an

1 interface material to prevent a pre-ceramic polymer resin
2 from adhering strongly to the reinforcing fibers, forming a
3 mixture of a pre-ceramic polymer resin and reinforcing
4 fibers coated with the interface material, forming an
5 exhaust manifold shaped structure from the mixture of the
6 pre-ceramic polymer resin and the reinforcing fibers coated
7 with the interface material by placing the mixture on at
8 least a portion of the cast monolithic ceramic material,
9 and firing the exhaust component shaped structure at a
10 temperature and a time sufficient to convert the pre-ceramic
11 polymer resin to a ceramic thereby forming a reinforced
12 ceramic composite.

13 U. S. Patent No. 5,153,295 teaches compositions of
14 matter that have potential utility as precursors to silicon
15 carbide. These compositions are obtained by a Grignard
16 coupling process. The process starts from chlorocarbo-
17 silanes and a readily available class of compounds. The new
18 precursors constitute a fundamentally new type of polycarbo-

1 silane that is characterized by a branched, $[\text{Si}-\text{C}]_{\text{sub.n}}$
2 "backbone" which consists of $\text{SiR}_{\text{sub.3}}\text{CH}_{\text{sub.2}}--$, $--$
3 $\text{SiR}_{\text{sub.2}}\text{CH}_{\text{sub.2}}--$, $\text{.dbd.SiRCH}_{\text{sub.2}}--$, and
4 $\text{.tbd.SiCH}_{\text{sub.2}}--$ units (where R is usually H but can also
5 be other organic or inorganic groups, e.g., lower alkyl or
6 alkenyl, as may be needed to promote crosslinking or to
7 modify the physical properties of the polymer or the
8 composition of the final ceramic product). A key feature of
9 these polymers is that substantially all of the linkages
10 between the Si-C units are "head-to-tail", i.e., they are
11 Si to C. The polycarbosilane " $\text{SiH}_{\text{sub.2}}\text{CH}_{\text{sub.2}}$ " has a
12 carbon to silicon ratio of 1 to 1 and where substantially
13 all of the substituents on the polymer backbone are
14 hydrogen. This polymer consists largely of a combination of
15 the four polymer "units": $\text{SiH}_{\text{sub.3}}\text{CH}_{\text{sub.2}}--$, $--\text{SiH}_{\text{sub.2}}$
16 $\text{CH}_{\text{sub.2}}--$, $\text{.dbd.SiHCH}_{\text{sub.2}}--$, and $\text{.tbd.SiCH}_{\text{sub.2}}--$
17 which are connected "head-to-tail" in such a manner that a
18 complex, branched structure results. The branched sites

1 introduced by the last two "units" are offset by a
2 corresponding number of SiH.sub.3 CH.sub.2 -- "end groups"
3 while maintaining the alternating Si--C "backbone". The
4 relative numbers of the polymer "units" are such that the
5 "average" formula is SiH.sub.2 CH.sub.2. These polymers
6 have the advantage that it is only necessary to lose
7 hydrogen during pyrolysis, thus ceramic yields of over 90%
8 are possible, in principle. The extensive Si--H
9 functionality allows facile crosslinking and the 1 to 1
10 carbon to silicon ratio and avoids the incorporation of
11 excess carbon in the SiC products that are ultimately
12 formed. The synthetic procedure employed to make them
13 allows facile modification of the polymer, such as by
14 introduction of small amounts of pendant vinyl groups, prior
15 to reduction. The resulting vinyl-substituted "SiH.sub.2
16 CH.sub.2 " polymer has been found to have cross-linking
17 properties and higher ceramic yield.

18 A pre-ceramic polymer is prepared by a thermally

1 induced methylene insertion reaction of polydimethylsilane.
2 The resulting polymer is only approximately represented by
3 the formula $[\text{SiHMeCH}_2]_n$, as significant amounts of
4 unreacted $(\text{SiMe}_2)_n$ units, complex rearrange-ments,
5 and branching are observed. Neither the preparation nor the
6 resulting structure of this precursor is therefore similar
7 to the instant process. In addition to the carbosilane
8 "units", large amounts of Si--Si bonding remains in the
9 "backbone" of the polymer. This polymer, in contrast to the
10 instant process, contains twice the stoichiometric amount of
11 carbon for SiC formation. The excess carbon must be
12 eliminated through pyrolytic processes that are by no means
13 quantitative. Despite the shortcomings, this polymer has
14 been employed to prepare "SiC" fiber. However, it must be
15 treated with various crosslinking agents prior to pyrolysis
16 which introduce contaminants. This results in a final
17 ceramic product that contains significant amounts of excess
18 carbon and silica that greatly degrade the high temperature

1 performance of the fiber.

2 SiC precursors predominately linear polycarbo-silanes
3 have been prepared via potassium dechlorination of chloro-
4 chloromethyl-dimethylsilane. The resulting polymers have
5 not been fully characterized, but probably contain
6 significant numbers of Si--Si and CH₂--CH₂ groups
7 in the polymer backbone. The alkali metal dechlorination
8 process used in the synthesis of such materials does not
9 exhibit the selective head-tail coupling found with Grignard
10 coupling. The pendant methyl groups in such materials also
11 lead to the incorporation of excess carbon into the system.
12 In several polymer systems mixtures containing vinylchloro-
13 silanes (such as CH₂.dbd.CH--Si(Me)Cl₂) and
14 Me₂SiCl₂ are coupled by dechlorination with
15 potassium in tetrahydro-furan. U. S. Patent No. 4,414,403
16 and U. S. Patent No. 4,472,591 both teach this method. The
17 "backbone" of the resulting polymers consists of a
18 combination of Si--Si and Si--CH₂ CH(--Si)₂ units.

1 Later versions of this polymer $\text{Me}(\text{H})\text{SiCl}_{1.2}$ in addition
2 to the $\text{Me}_{1.2}\text{SiCl}_{1.2}$ and are subjected to a sodium-
3 hydrocarbon dechlorination process which does not attack
4 vinyl groups. The resulting polymer consists of a
5 predominately linear, Si-Si "backbone" bearing pendant
6 methyl groups, with some Si-H and Si-CH₂CH₂
7 functionality to allow crosslinking on pyrolysis.

8 None of these precursors derived using vinylchloro-
9 silanes are similar to those of the process in that having
10 predominantly Si-Si bonded "backbones", they are
11 essentially polysilanes, not polycarbosilanes. In addition,
12 the carbon in these polymers is primarily in the form of
13 pendant methyl functionality and is present in considerable
14 excess of the desirable 1 to 1 ratio with silicon. The
15 ceramic products obtained from these polymers are known to
16 contain considerable amounts of excess carbon.

17 Polymeric precursors to SiC have been obtained by
18 redistribution reactions of methyl-chloro-disilane

1 (Me.sub.6-x Cl.sub.x Si.sub.2, x=2-4) mixtures, catalyzed by
2 tetraalkyl-phosphonium halides which U. S. Patent No.
3 4,310,481, U. S. Patent No. 4,310,482 and U. S. Patent No.
4 4,472,591 teach. In a typical preparation, elemental
5 analysis of the polymer was employed to suggest the
6 approximate formula [Si(Me).sub.1.15 (H).sub.0.25].sub.n,
7 with n averaging about 20. The reaction is fundamentally
8 different than that involved in the process and the
9 structures of the polymers are also entirely different,
10 involving what is reported to be a complex arrangement of
11 fused polysilane rings with methyl substitution and a
12 polysilane backbone.

13 The formation of carbosilane polymers with pendent
14 methyl groups as by-products of the "reverse-Grignard"
15 reaction of chloromethyl-dichloro-methylsilane. The chief
16 purpose of this work was the preparation of carbosilane
17 rings and the polymeric byproduct was not characterized in
18 detail nor was its use as a SiC precursor suggested.

1 Studies of this material indicate that it has an
2 unacceptably low ceramic yield on pyrolysis. These polymers
3 are related to those described in the instant process and
4 are obtained by a similar procedure, however, they contain
5 twice the required amount carbon necessary for
6 stoichiometric silicon carbide and their use as SiC
7 precursors was not suggested. Moreover, the starting
8 material, chloromethyl-dichloro-methylsilane, contains only
9 two sites on the Si atom for chain growth and therefore
10 cannot yield a structure which contains SiCH_2 --
11 chain units. On this basis, the structure of the polymer
12 obtained, as well as its physical properties and pyrolysis
13 characteristics, must be significantly different from that
14 of the subject process.

15 U. S. Patent No. 4,631,179 teaches a polymer which is
16 a product of the ring-opening polymerization of $(\text{SiH}_2$
17 $\text{CH}_2)_2$ also has the nominal composition " SiH_2
18 CH_2 ". However, the actual structure of this polymer

1 is fundamentally and functionally different from that of the
2 instant process. Instead of a highly branched structure
3 comprised of SiR_3CH_2 --, $\text{--SiR}_2\text{CH}_2$ --,
4 .dbd.SiRCH_2 --, and .tbd.SiCH_2 -- units, the Smith
5 polymer is reported to be a linear polycarbosilane which
6 presumably has only $[\text{SiH}_2\text{CH}_2]$ as the internal
7 chain segments. Such a fundamental structural difference
8 would be expected to lead to quite different physical and
9 chemical properties. The fundamental difference in these
10 two structures has been verified by the preparation of a
11 linear polymer analogous to polymer and the comparison of
12 its infrared and H-NMR spectra.

13 Another important difference between the process of
14 Smith and the instant process is the method used to obtain
15 the product polymer and the nature of the starting
16 materials. The $[\text{SiH}_2\text{CH}_2]_n$ monomer used by
17 Smith is difficult and expensive to prepare and not
18 generally available, whereas the chlorocarbosilanes used in

1 the instant process are readily available through commercial
2 sources.

3 U. S. Patent No. 4,923,716 teaches chemical vapor
4 deposition of silicon carbide which uses a "single
5 molecular species" and which provides reactive fragments
6 containing both silicon and carbon atoms in equal number
7 this process. Linear and cyclic structures of up to six
8 units are mentioned. These compounds, which include both
9 silanes and carbosilanes, are specifically chosen to be
10 volatile for chemical vapor deposition use, and are
11 distinctly different from the instant process, where the
12 products are polymers of sufficiently high molecular weight
13 that they cross-link before significant volatilization
14 occurs. Such volatility would be highly undesirable for the
15 applications under consideration for the polymers of the
16 instant process, where excessive loss of the silicon-
17 containing compound by vaporization on heating would be
18 unacceptable.

1 The inventors hereby incorporate the above-referenced
2 patents and articles into this application.

3 SUMMARY OF THE INVENTION

4 The present invention is generally directed to a
5 process of forming hafnium carbide that is derived from a
6 preceramic polymer.

7 In a first separate aspect of the invention the hafnium
8 nitride contains a ceramic fiber derived from a preceramic
9 polymer.

10 In a second separate aspect of the invention the
11 hafnium contains preceramic polymer derived from the
12 reaction of a hafnium containing halide compound and an
13 amine containing organic compound.

14 In a third separate aspect of the invention the
15 preparation of a hafnium contains preceramic polymer through
16 the reaction of hafnium halide compound with any of the
17 following compounds: ethylene diamine, dimethyl ethylene
18 diamine, piperazine, allylamine, or polyethylene-imine.

1 In a fourth separate aspect of the invention the
2 production of a hafnium carbide containing ceramic fiber
3 consists of the steps of melting a hafnium containing
4 preceramic polymer, extruding said polymer through an
5 orifice to form fiber, cross-linking said fiber and heating
6 the cross-linked fiber under controlled atmospheric
7 conditions at a temperature greater than 600 degrees
8 centigrade to obtain a hafnium carbide containing ceramic
9 fiber.

10 In a fifth separate aspect of the invention the
11 production of a hafnium nitride containing ceramic fiber
12 consists of the steps of melting a hafnium containing
13 preceramic polymer, extruding said polymer through an
14 orifice to form a fiber, cross-linking said fiber and
15 heating the cross-linked fiber under in an ammonia
16 containing atmosphere at a temperature greater than 600
17 degrees centigrade to obtain a hafnium nitride containing
18 ceramic fiber.

1 Other aspects and many of the attendant advantages will
2 be more readily appreciated as the same becomes better
3 understood by reference to the following detailed
4 description.

5 The features of the present invention which are
6 believed to be novel are set forth with particularity in the
7 appended claims.

8 DESCRIPTION OF DRAWINGS

9 Fig. 1 is schematic drawing of an apparatus for making
10 flat plates of ceramic composites from photo-curable pre-
11 ceramic polymers.

12 Fig. 2 is schematic drawing of an apparatus for making
13 cylinders of ceramic composites from photo-curable pre-
14 ceramic polymers.

15 Fig. 3 is a graphical representation of melting points
16 of high temperature refractory metals and ceramics that has
17 been taken from Jaffee, R. and Maykuth, D. J., "Refractory
18 Materials", Battelle Memorial Institute, Defense Metals

1 Information Center, Memo 44, 1960.

2 Fig. 4 is schematic diagram of a molecular level Hf, C,
3 & N mixing that could result in suppression of exaggerated
4 grain growth at high temperatures. Also, better adherence of
5 oxide layer.

6 Fig. 5 is a photograph of a HfCN Nanocomposite Powder
7 Derived from PPHZ Heat Treated to 1200 degrees centigrade
8 under flowing Nitrogen.

9 Fig. 6 is schematic diagram of a reaction scheme of
10 hafnium chloride with ethylene-diamine.

11 Fig. 7 is schematic diagram of structures of HfCN
12 preceramic polymer network formers.

13 Fig. 8 is schematic diagram at high temperature of
14 linear HfCN polymers begin to cross-link. Further increased
15 temperature increases thermal decomposition and, as a
16 result, the polymer structure rearranges to form HfCN
17 ceramic.

18 Fig. 9 is a photograph of a fiber being extruded from

1 pressurized dye at 120 degrees centigrade.

2 Fig. 10 is a schematic diagram of an optical micrograph
3 of optically transparent preceramic polymer fiber.

4 Fig. 11 is schematic diagram of a scanning electron
5 photomicrograph of a $\text{Si}_3\text{N}_4/\text{SiC}$ (SiNC) ceramic fiber heat-
6 treated under nitrogen at 1200 degrees centigrade.

7 Fig. 12 is a graph of fiber strength as a function of
8 fiber diameter that has been reproduced from Raj, R.,
9 Riedel, R., Soraru, G.D., "Introduction to the Special
10 Topical Issue on Ultrahigh-Temperature Polymer-Derived
11 Ceramics", J. Amer. Ceram. Soc., vol. 84[10] (2001) pp.2158-
12 59.

13 Fig. 13 is schematic diagram of fluorescence emission
14 of preceramic polymer.

15 Fig. 14 is schematic diagram of a scanning electron
16 micrograph of HfC ceramic fiber.

17 Fig. 15 is schematic diagram of addition of curable
18 ethynyl side groups onto polymer backbone.

1 DESCRIPTION OF THE PREFERRED EMBODIMENT

2 A continuous single step manufacturing process for
3 fabricates dense low-porosity composites using novel cross-
4 linkable pre-ceramic polymers and simple plastic industry
5 technology adapted to the thermoset capability of the pre-
6 ceramic polymer. The process eliminates the multi-cycle
7 polymer impregnation pyrolysis method. The process is a
8 simple controllable production process for fiber reinforced
9 ceramic matrix composites, which can be easily automated
10 into large manufacturing continuous processes. This process
11 combines high-yield cross-linkable pre-ceramic polymers and
12 a single step automated process mechanism to produce ceramic
13 components on the scale of aircraft fuselages, boat hulls,
14 and large single ceramic sheets for space vehicle skin
15 panels. The process provides chemically modified pre-
16 ceramic polymers which are very fluid at temperatures 60° C-
17 100° C, have high ceramic yields by weight of 75-95%,
18 exhibit high purity and can be crosslinked into a thermoset

1 with ultraviolet radiation. The process achieves by a
2 series of chemical substitutions using commercially
3 available polymers to incorporate ethynyl side groups on the
4 polymers, which then contain unstable carbon triple bonds
5 and cross-link, by hydrosilylation with Si-H groups upon
6 photo-exposure. The process is to use the chemical
7 substitution ethynyl side group chemistry to produce SiC,
8 Si₃N₄, Al₂O₃ and Al₃N₄ and TiC upon pyrolysis after photo-
9 exposure. Conversion of precursor polymers like
10 polycarbosilane and polysilazane to poly(ethynyl)-
11 carbosilane and poly(ethynyl)silazane achieve this
12 objective. The process draws a fiber, tape, fabric, woven
13 cloth onto a mandrel or suitable substrate by first passing
14 it through the chemically modified pre-ceramic polymer. The
15 objective of this process is to saturate the fiber, tape,
16 fabric, woven cloth with the very fluid pre-ceramic polymer
17 and then photo-cure it on the mandrel or substrate as the
18 saturated material is drawn along by motorized winding or

1 pulling mechanisms known to the prior art. The process
2 provides a continuous fabrication process to enable making a
3 dense (total porosity <8%) fiber reinforced ceramic
4 composite in a single step. This objective is achieved by
5 compacting each layer of pre-ceramic polymer saturated
6 material onto the already pyrolyzed layer below permitting
7 excess polymer to impregnate this layer. The back-fill
8 allowed here reduces the final component porosity, increases
9 strength and provides a short path for volatiles to escape
10 mitigating interlayer delamination. This layer by layer
11 buildup is continued until the required component thickness
12 is reached.

13 The novel nature of the photocurable pre-ceramic
14 polymer enables a process, which is unique to porous filters
15 not achievable with conventional pre-ceramic polymers. This
16 process employs the ability to thermoset the pre-ceramic
17 polymer into a rubbery hard solid prior to heating. In this
18 form the pre-ceramic polymer can be heated and subsequently

1 pyrolyzed without flowing into unwanted areas of the filter.
2 Because of the ability of this process to produce high yield
3 beta-SiC in near Si-C stoichiometry a matrix or coating is
4 formed upon sintering that is highly receptive to heating
5 with microwave energy. The microwave susceptible porous
6 filter is ideally suited for trapping particulate from
7 diesel engine exhausts and can be regeneratively used by
8 microwave heating to a temperature above the oxidation
9 threshold of the trapped particulate soot. The pre ceramic
10 polymer can be made to form not only SiC but also other
11 ceramic bodies such as Si_3N_4 , BC, LAS, etc.

12 Referring to Fig. 1 an apparatus 10 for making flat
13 plates of ceramic composites from photo-curable pre-ceramic
14 polymers includes a frame 11 with a process bed, a set of
15 fabric rollers 12, a set of guide rollers 13, a set of drive
16 rollers 14, a drive motor 15, a compression roller 16, a
17 process head 17 having a light-emitting lamp, a furnace 18,
18 a covering 19 and a source of inert gas and a control panel

1 20. The source of inert gas provides an inert atmosphere.

2 Referring to Fig. 2 an apparatus 110 for making
3 cylinders of ceramic composites from photo-curable pre-
4 ceramic polymers includes a dry nitrogen environmental
5 chamber 111, a fabric roller 112, an applicator 113 of a
6 photo-curable pre-ceramic polymer, a take-up mandrel 114, a
7 pressure loaded compaction roller 115, a light-emitting lamp
8 116 and a consolidation and pyrolysis zone 117. The
9 consolidation and pyrolysis zone 117 has a heater 118. The
10 fabric roller dispenses woven ceramic fabric.

11 Commercially available polycarbosilanes and
12 polycarbosiloxane polymers could be rendered photo-curable,
13 by high intensity photo-radiation, through the addition of
14 ethynyl side groups to the polymer. The polymer,
15 poly(ethynyl) carbosilane, is rendered into an infusible
16 thermoset upon photo-radiation. The process is able to
17 similarly elevate ceramic yields to ~85 % by weight.

1 It has been demonstrated that various combinations of
2 di-functional and tri-functional silane precursors can be
3 utilized to enhance cross-linking and elevate ceramic yield.
4 Combinations of dichlorodimethylsilane (di-functional) and
5 trichlorophenylsilane (tri-functional) can be employed.
6 Through the addition of branching, or cross-linking, ceramic
7 yields as high as 77% have been obtained. Further, it is
8 possible to doped these polymers, with boron for example, to
9 control sintering and crystallization behavior.

10 While this process allows the addition of ethynyl side
11 groups to potentially a wide range of available pre-ceramic
12 polymers, there are other methods of directly synthesizing
13 poly(ethynyl)carbosilane, which are outlined below. In both
14 of the following reaction paths, tri-functional organotri-
15 chlorosilanes are utilized, in part or in entirety, to
16 permit the introduction of photo-polymerizable side-groups,
17 such as ethynyl groups derived from the reaction of sodium
18 acetylide with chlorosilane.

1 In the first reaction route, sodium acetylide is
2 reacted with the organotrichlorosilane, such as a methyl- or
3 phenyltrichlorosilane, as shown in step 1. Typically, this
4 is performed in a solvent, such as hexane or methylene
5 chloride. The by-product of this reaction is sodium
6 chloride, which is insoluble and can be easily removed by
7 filtration and/or sedimentation. The resulting
8 organo(ethynyl)chlorosilane can be reacted directly with
9 sodium which is a Würtz type condensation reaction or mixed
10 with an organodichlorosilane prior to the initiation of
11 polycondensation. Assuming that all "R"s are the same, and
12 "a + b = 1", then the following reaction path can be
13 proposed:

Processing Step	Reaction
1. The addition of ethynyl (acetylide) side groups to tri-functional polysilazane	$a \{ \text{RSiCl}_3 + g \text{ NaC}\equiv\text{CH} \rightarrow$ $\text{RSiCl}_{(3-g)}\text{C}\equiv\text{CH}_g + g \text{ NaCl} \}$

functional polysilazane reactant.	
2. Remove NaCl by filtration.	- ag NaCl
3. The addition of di-functional chain former (optional).	+ b {R ₂ SiCl ₂ }
4. Condensation of modified precursor solution to produce poly(ethynyl)silazane pre-ceramic polymer through the addition of sodium.	$a(RSiCl_{(3-g)}C\equiv CH_g) + b(R_2SiCl_2) + 2[a(3-g) + b]Na \rightarrow 1/n\{Si_{(a+b)}R_{(a+2b)}C\equiv CH_{ag}\}_n + 2[a(3-g) + b]NaCl$

Table 1: New processing route 1: Steps and reaction chemistries to form poly(ethynyl)carbosilane-- Final Product = $1/n\{SiR_{(a+2b)}C\equiv CH_{ag}\}_n$.

1 In route 1, the photo-cross-linkable ethynyl group
2 (acetylide) is added prior to the initiation of Würtz type
3 condensation reaction. In route 2, a method of adding
4 ethynyl side-groups post-condensation, thereby avoiding the
5 exposure of the ethynyl ligand to sodium during the pre-
6 ceramic polymer synthesis is disclosed. In this process,
7 tri-functional and/or a mixture of di-functional and tri-
8 functional chlorosilanes are reacted with a sub-
9 stoichiometric quantity of metallic sodium, sufficient to
10 bring about an increase in molecular weight and viscosity of
11 the now pre-ceramic polymer backbone, but leaving a fraction
12 of the chlorosilane reaction sites unreacted. The resulting
13 sodium chloride by-product can be removed by filtration
14 and/or sedimentation (step 2).

15 Following polymer condensation, with unreacted
16 chlorosilane sites intact, excess sodium acetylide is added
17 to react with the aforementioned unreacted sites to produce
18 poly(ethynyl)carbosilane photo-curable pre-ceramic polymer.

1 The poly(ethynyl)carbosilane pre-ceramic polymer can be
 2 retrieved by solvent evaporation by the application of heat
 3 and/or in vacuo. Assuming that all "R"s are the same, and
 4 "a + b = 1", the final desired reaction product is expressed
 5 in the reaction path below in Table 2.
 6 Table 2: New processing route 2: Steps, and reaction
 7 chemistries, to form poly(ethynyl)carbosilane.

Processing Step	Reaction
1. Mixture of di-functional and tri-functional chlorosilanes reacted with a sub-stoichiometric amount of sodium (where $y < [3a+2b]$).	$a(RSiCl_3) + b(R_2SiCl_2) + [y/(3a+2b)]Na \rightarrow$ $(1/n) \{ Si_{(a+b)} R_{(a+2b)} Cl_{[(1-y)/(3a+2b)]} \}_n +$ $[y/(3a+2b)] NaCl$
2. Remove NaCl by	$-[y/(3a+2b)] NaCl$

filtration and/or sedimentation.	
3. Addition of ethynyl side groups to partially condensed polysilazane polymer through the addition of excess sodium acetylide.	$ \begin{aligned} & (1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{Cl}_{[(1-y)/(3a+2b)]} \}_n \\ & + [(1-y)/(3a+2b)] \text{NaC}\equiv\text{CH} \rightarrow \\ & (1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n + \\ & [(1-y)/(3a+2b)] \text{NaCl} \end{aligned} $

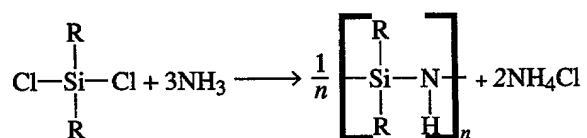
Product = $(1/n) \{ \text{SiR}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n$.

- 1 In the previous section, the method of preparing
- 2 poly(ethynyl)carbosilane, a photo-curable pre-ceramic
- 3 polymer precursor to silicon carbide has been reviewed. In
- 4 this section, several of the promising methods of
- 5 synthesizing polysilazane precursors to silicon nitride
- 6 (Si_3N_4) and a method of conversion to poly(ethynyl)silazane,
- 7 a photo-curable pre-ceramic polymer precursor to high yield

1 $\text{Si}_3\text{N}_4/\text{SiC}$ ceramic matrix composites are described. Si_3N_4
2 doped with 10-15 weight percent SiC has significantly lower
3 creep at high temperature than pure Si_3N_4 . The creep rate
4 at the minimum was lower by a factor of three than that of
5 the unreinforced, monolithic matrix of equal grain size.
6 Thus, other researchers have recognized the potential
7 importance of $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposite matrices for
8 continuous ceramic fiber reinforced composites used in high
9 temperature applications. Two advantages of the process of
10 the process are the ability to fabricate large-scale
11 composites employing existing polymer composite fabrication
12 techniques due to the addition of the photo-cross-linkable
13 ethynyl side-groups and the inclusion of the carbon
14 containing ethynyl group should lead to the addition of
15 approximately 5 to 20 weight percent SiC upon pyrolysis.

16 One of the simplest and direct methods of preparing
17 polysilazane precursors to silicon nitride, with a 70 weight
18 percent ceramic yield is to dissolve dichlorosilane in

1 dichloromethane to yield polysilazane oils. Pyrolysis in
 2 flowing nitrogen gas yielded nearly phase pure α - Si_3N_4 after
 3 heat treatment at 1150°C for 12 hours. Numerous other
 4 permutations and refinements to the preparation of
 5 polysilazane oils and polymers have been developed. The
 6 reaction path of polysilazane formation using
 7 dichlorosilanes and ammonia is set out below:



8
 9 A number of the most direct permutations include the
 10 use of trichlorosilanes, methyltrichlorosilanes, dimethyl-
 11 dichlorosilanes, and vinyl-, butyl-, phenyl-, ethyl-, and
 12 hexyl- modified chlorosilanes. Increased molecular weight,
 13 and correspondingly increased ceramic yield, can be achieved
 14 by catalytically enhancing the cross-linking during final
 15 polymer preparation. A number of novel methods, including
 16 the use of ruthenium compounds and potassium hydride have

1 been demonstrated to give ceramic yields upon pyrolysis as
2 high as 85 percent. The inducement of cross-linking prior
3 to pyrolysis is essential to achieving the high ceramic
4 yields necessary to large-scale commercialization of Si_3N_4
5 matrix composites for high temperature applications. The
6 cross-linking methods cited in the literature, however, are
7 chemical catalysts, making the shaping and forming processes
8 extremely difficult.

9 A ceramic matrix of predominantly silicon nitride with
10 about 10-15 % SiC by weight is nearly ideal for fabricating
11 CMCs. In addition, the catalytic cross-linking of the
12 polysilazane precursor dramatically increases ceramic yield.

13 The synthesis route should produce high yield $\text{Si}_3\text{N}_4/\text{SiC}$
14 nanocomposites employing a photocurable pre-ceramic polymer
15 precursor.

16 One possible method would be to synthesize the
17 unmodified polysilazane through the ammonolysis of various
18 chlorosilane reactants in dichloromethane solvent followed

1 by modifying the resulting polysilazanes, using a previously
 2 described process of chlorination followed by attachment of
 3 the ethynyl through reaction with sodium acetylide. An
 4 alternative approach starts with a variety of dichloro-
 5 silanes and/or trichlorosilanes and reacts them with sodium
 6 acetylide at various concentrations, followed by ammonolysis
 7 to result in the final poly(ethynyl) silazane precursor as
 8 specifically detailed in the Table 3 below:

Processing Step	Reaction
1. addition of acetylide side groups trifunctional polysilazane reactant.	$a \{ \text{RSiCl}_3 + g \text{ NaCCH} \rightarrow \text{RSiCl}_{(3-g)}\text{CCH}_g + g \text{ NaCl} \}$
2. remove NaCl by filtration	$- g \text{ NaCl}$
2. addition of difunctional chain former	$b \{ \text{R}_2\text{SiCl}_2 \}$
3. ammonolysis of modified	$a [\text{RSiCl}_{(3-g)}\text{CCH}_g] + b [\text{R}_2\text{SiCl}_2] + \text{NH}_3$

precursor solution to produce poly(ethynyl)silazane pre- ceramic polymer	$\rightarrow b\{[\text{SiR}_2(\text{NH})]_n\} + a\{[\text{RSi}(\text{NH})_{(3-g)}\text{CCH}_g]_m\} + 2[a(3-g) + 2b]\text{NH}_4\text{Cl}$
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Table 3: Processing steps and reaction chemistries to form poly(ethynyl)silazane

1 The following are examples of combining commercially
2 available polymers and catalysts to achieve a final photo-
3 curable pre-ceramic polymer to SiC ceramics. In order to be
4 photo-curable, the polymer requires either double-bonded
5 carbons such as Allyl side groups or triple-bonded carbons
6 such as acetylide or propargyl side groups. The catalysts
7 can include a thermally curable component such as benzoil
8 peroxide and a photo-curable initiator such as Ciba-Geigy's
9 Irgacure 1800TM or a combination of camphorquinone and 2-
10 (dimethylamino)- ethyl methacrylate).
11 MATECH Advanced Materials began a small IR&D program to
12 extend our family of photocurable preceramic polymers to

1 HfCN nanocomposite ceramics. We have begun synthesizing
2 poly(propyl)hafnizane (PPHZ) and poly(ethynyl)hafnizane
3 (PEHZ) preceramic polymers. Both low molecular weight and
4 high molecular weight polymers have been demonstrated. Upon
5 pyrolysis at 1200 degrees centigrade in flowing nitrogen,
6 the ceramic yield has been measured at as high as 74 % by
7 weight. A photograph of the dark grey psuedo-amorphous HfCN
8 nanocomposite powder produced from the pyrolysis of PPHZ at
9 1200 degrees centigrade is shown in Fig. 5. Through careful
10 control of molecular weight, as has been demonstrated for
11 our preceramic polymers to SiC and Si₃N₄, we believe we can
12 tailor the viscosity for coating, fiber, and matrix
13 infiltration applications.

14 Substantial effort has been assigned to develop
15 effective methods for making advanced ceramic matrix
16 composites using pre-ceramic polymers. This method is very
17 successful so far for manufacturing silicon based composite
18 materials like silicon carbide, silicon nitride, and silicon

1 oxycarbide. Similar work has been done to produce
2 organometallic precursors for the transition metal carbides,
3 however with much more difficulties. Relatively few
4 compounds of the hafnium metal are stable, do not contain
5 oxygen and have a low carbon to metal ratio. Most compounds
6 are easily sublimated, leading to a low ceramic yields upon
7 pyrolysis.

8 Referring to Fig. 3 the desirable properties of HfC and
9 HfN for ultra high temperature applications has been well
10 recognized. Hafnium carbides high melting temperature has
11 been known for decades. Hafnium carbide and nitride is
12 conventionally prepared by hot-pressing to obtain monolithic
13 HfC ceramics and CVD to obtain coatings. Currently, there
14 are no examples of hafnium carbide fibers either
15 commercially available or being developed for research. In
16 the late 1980's, there was a brief program at Refractory
17 Composites, Inc. (Whittier, CA) under the direction of Jim
18 Warren to produce HfC fibers by chemical vapor deposition

1 (CVD) onto carbon monofilaments, which was prohibitively
2 expensive and unsuccessful. No HfC or HfN fibers have ever
3 been prepared from preceramic polymers. Commercial
4 applications for HfCN structural ceramic fibers and matrices
5 include, but are not limited to, the following commercial
6 and military solid rocket motor nozzle liner and nozzle
7 components, liquid rocket combustors and nozzle extensions;
8 liquid rocket tankage and lines, liquid rocket turbo-pump
9 components, tactical missile canister systems and hypersonic
10 leading edges.

11 Hafnium carbide is the most refractory binary
12 composition known, with a melting point cited at from
13 between 3890 to as high as 4160 degrees centigrade. Hafnium
14 nitride is also the most refractory of all nitrides, with a
15 melting point of 3307 degrees centigrade. For this reason,
16 hafnium carbide and hafnium nitride have been proposed for
17 very high temperature applications, such as zero erosion
18 rocket nozzle throats and even as filaments in incandescent

1 light bulbs. Hafnium carbide has a high thermal
2 conductivity (292.88 W/moC) as does hafnium nitride (117.15
3 W/moC). Therefore, a mixed hafnium carbide/nitride
4 nanocomposite should possess both a high melting point and
5 high thermal conductivity. Selected properties of hafnium
6 carbide, -nitride, and other materials are compared in Table
7 1. The melting points of a large selection of metals and
8 ceramics are compared in Fig. 5 for convenience.

9 Most potential starting materials of hafnium polymer
10 precursors are expensive. To have a financially competitive
11 synthetic method to make hafnium carbide, nitride or its
12 ceramic compositions requires some high degree of design.
13 The availability of hafnium containing, oxygen free starting
14 materials is principally limited to hafnium halides and
15 their bis(cyclopentadienyl) analogues. The only cost
16 effective starting material is hafnium chloride. There are
17 many theoretically possible bi-functional, commercially
18 available, economically appropriate linkers to form

1 "organic backbone" between hafnium atoms.

2 In preliminary experiments to synthesize preceramic
3 polymers to HfCN, ethylene-diamine(EDA), dimethyl-ethylene-
4 diamine(DMEDA), piperazine, allylamine, and poly-
5 ethyleneimines were used to form the polymer backbone by
6 reaction with hafnium tetra-chloride. The structures for
7 these polymer network formers are presented in Fig. 7.

8 When reacting two starting materials, a very exothermic
9 reaction occurred and the liquid mixture solidified. When
10 the exothermic reaction was complete, the temperature was
11 increased to the melting point and slowly increased further
12 to obtain a homogenous, cross-linked polymer. Polymers were
13 fired at 1200 degrees centigrade to get HfCxNy ceramic.
14 Every step of the reaction was kept in an inert N2
15 atmosphere (<0.5 ppm oxygen and moisture).

16 Preliminary experiment results show the desired
17 nitrogen and hafnium content, however, excess free carbon
18 and some oxygen contamination was present. While these

1 preliminary results are encouraging, further optimization of
2 the reaction parameters are necessary. The relatively low
3 ceramic yield is due to a lack of cross-linking and
4 sublimation. In the reaction, chloride is released in the
5 form of hydrochloride which forms salt with amine groups of
6 the amine containing reactant. Organic hydrochloride salts
7 have tendency to sublime or decompose before or around
8 their melting point.

9 More study is needed to find optimal conditions of
10 cross-linking, to understand the mechanism, and to avoid
11 salt formation in the polymer.

12 Preceramic polymers, that are solid at room
13 temperature, can be used to produce fiber by placing them in
14 a pressure tight containing with a small orifice at on end
15 and a gas inlet at the other. The chamber can be heated to a
16 determined temperature, usually between 70 to 220 degrees
17 centigrade, depending upon the molecular weight and
18 softening temperature of the polymer. Upon reaching fiber

1 drawing temperature, and after the polymer has thoroughly
2 melted, an inert gas is introduced into the top of the
3 chamber to a given pressure, usually between 2 and 20 pounds
4 per square inch, to force the polymer through the orifice
5 resulting in a fiber in Fig. 9. The fiber can then be wound
6 continuously on a take-up mandrel.

7 The melt-spun fibers are typically transparent or
8 lightly colored, as shown in Fig. 10. The preceramic
9 fibers, which include a photoinitiator, can then be cured by
10 exposure to ultraviolet light. After curing, the fibers can
11 then be pyrolyzed at elevated temperatures (typically
12 between 1100 degrees centigrade and 1600 degrees centigrade,
13 resulting in a dense, uniform structural ceramic fiber, an
14 example of which is shown in Fig. 11.

15 Of great importance in making structural ceramic fibers
16 is diameter control. As can be seen in Fig. 14, fiber
17 strength is greatly affected by diameter. For industrial
18 applications, fibers with diameters below 12 microns are

1 preferred.

2 Preceramic polymer fibers prepared from the reaction of
3 hafnium tetrachloride and ethylene-diamine, as described in
4 EXAMPLE 1 below, are shown in Fig. 13. Unlike other
5 preceramic polymers that have been developed, these fibers,
6 in addition to being photocurable, are also highly
7 fluorescent and phosphorescent. The photo-cured fibers can
8 be heat treated in either inert atmosphere, rendering a
9 black fiber that is principally composed of hafnium carbide
10 (HfC) and a minority phase of hafnium nitride (HfN). When
11 pyrolyzed under a flowing ammonia gas, the resulting fibers
12 are white and composed solely of hafnium nitride (HfN).

13 EXAMPLE 1

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoiniti ator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoiniti ator 2	None	None

EXAMPLE 2

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
RT initiator	N,N-dihydroxyparatoluidine	0.02

EXAMPLE 3

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.01
Photoinitiator 2	None	None

EXAMPLE 4

Category	Compound	Amount (grams)
Polymer	Poly(ethynyl)carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoinitiator 2	None	None

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EXAMPLE 5

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 6

Category	Compound	Amount (grams)
Polymer	Poly(ethynyl) carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 7

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	None
Photoinitiator 1	Camphorquinone	0.02

Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02
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EXAMPLE 8

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

EXAMPLE 9

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	none
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

- 1 All of the above examples cross-linked under photo-
- 2 irradiation (using either ultraviolet light or blue light as
- 3 indicated) within a few minutes to an hour under continuous
- 4 irradiation at room temperature. The samples were

1 transformed by this method from thermoplastic to thermoset
2 pre-ceramic polymers that did not flow or deform
3 significantly upon subsequent heat-treatment and pyrolysis,
4 ultimately yielding SiC containing ceramics. The examples
5 are meant to be illustrative. A person trained in the art
6 can easily modify the ratios and selection of both pre-
7 ceramic polymer and/or photo-initiators and catalyst
8 combinations.

9 This process enables the continuous manufacture of
10 fiber reinforced ceramic composites by the use of high
11 ceramic yield pre-ceramic polymers that are photo-curable to
12 a thermoset from a thermoplastic state. A composite in any
13 form or shape is fabricated by photo-curing each individual
14 layer of fiber with in-situ pyrolysis of the pre-ceramic
15 polymer impregnated into the fiber layer. The layer by
16 layer of fiber, fabric or woven cloth is pressure loaded to
17 press the thermoplastic polymer infiltrated fabric onto the
18 mandrel or flat substrate thereby permitting excess polymer

1 to impregnate the porous, already pyrolyzed, layer below.
2 This single step process allows a shorter mean free path for
3 volatiles to escape with less destruction than the removal
4 of organics from more massive parts, for consolidation of
5 each layer individually, and for increased layer to layer
6 bonding and improved inter-laminar shear strengths.

7 Silicon carbide (SiC) is one of several advanced
8 ceramic materials which are currently receiving considerable
9 attention as electronic materials, as potential replacements
10 for metals in engines, and for a variety of other
11 applications where high strength, combined with low density
12 and resistance to oxidation, corrosion and thermal
13 degradation at temperatures in excess of 1000° C are
14 required. Unfortunately, these extremely hard, non-melting
15 ceramics are difficult to process by conventional forming,
16 machining, or spinning applications rendering their use for
17 many of these potential applications problematic. In
18 particular, the production of thin films by solution

1 casting, continuous fiber by solution or melt spinning, a
2 SiC matrix composite by liquid phase infiltration, or a
3 monolithic object using a precursor-based binder/sintering
4 aid, all require a source of SiC which is suitable for
5 solution or melt processing and which possesses certain
6 requisite physical and chemical properties which are
7 generally characteristic of polymeric materials.

8 Polymeric precursors to ceramics such as SiC afford a
9 potential solution to this problem as they would allow the
10 use of conventional processing operations prior to
11 conversion to ceramic. A ceramic precursor should be
12 soluble in organic solvents, moldable or spinnable,
13 crosslinkable, and give pure ceramic product in high yield
14 on pyrolysis. Unfortunately, it is difficult to achieve all
15 these goals simultaneously. Currently available SiC
16 precursor systems are lacking in one or more of these areas.
17 Problems have been encountered in efforts to employ the
18 existing polysilane and polycarbosilane precursors to SiC

1 for preparation of SiC fiber and monolithic ceramic objects.
2 All of these precursors have C/Si ratios considerably
3 greater than one, and undergo a complex series of ill-
4 defined thermal decomposition reactions which generally lead
5 to incorporation of excess carbon. The existence of even
6 small amounts of carbon at the grain boundaries within SiC
7 ceramics has been found to have a detrimental effect on the
8 strength of the ceramic, contributing to the relatively low
9 room-temperature tensile strengths typically observed for
10 precursor-derived SiC fibers.

11 Efforts to develop polymeric precursors to SiC have
12 focused largely on two types of polymers, polysilanes, which
13 have a Si--Si backbone, and polycarbosilanes, in which the
14 polymer backbone is $[-\text{Si}-\text{C}-]_n$. The polysilanes all
15 suffer from problems due to insolubility, infusibility
16 and/or excess carbon incorporation. Certain of the
17 polycarbosilanes have more suitable physical properties for
18 processing. These also contain a higher-than-1:1 C:Si ratio

1 and incorporate excess carbon on pyrolysis.

2 In the case of the polycarbosilanes, high molecular
3 weight linear polymers of the type $[R_{\text{sub.2}}SiCH_{\text{sub.2}}$
4 $]_{\text{sub.n}}$, where R is H and/or hydrocarbon groups, have been
5 prepared by ring-opening-polymerization reactions starting
6 from cyclic disilacyclobutanes using chloroplatinic acid and
7 related catalyst systems; however, such linear polycarbo-
8 silanes generally exhibit low yields of ceramic product on
9 pyrolysis due to chain "unzipping" reactions. For example,
10 studies of high molecular weight $[Me_{\text{sub.2}}SiCH_{\text{sub.2}}$
11 $]_{\text{sub.n}}$ polymers have indicated virtually complete
12 volatilization on pyrolysis under an inert atmosphere to
13 1000° C.

14 Use of propargyl groups (HC=CCH₂-), such as propargyl
15 chloride (HC=CCH₂Cl), propargyl bromide (HC=CCH₂Br),
16 propargyl alcohol (HC=CCH₂OH), propargyl magnesium chloride
17 (HC=CCH₂MgCl), propargyl calcium chloride (HC=CCH₂CaCl),
18 propargyl amine (HC=CCH₂NH₂), and other propargyl

1 containing species introduces the photo-curable
2 (Cross-linkable) triple-bonded carbon linkages into the pre-
3 ceramic polymer.

4 U. S. Patent No. 5,153,295 teaches the use of ceramic
5 polymers with an Si-C backbone structure, such as
6 allylhydridopolycarbosilane (AHPCS), formed from the
7 Grignard coupling reaction of a halomethylcarbosilane
8 followed by reduction using a metal hydride in which either
9 a UV cross-linkable ethynyl (i.e. acetylide) or propargyl
10 group has been introduced into the polymer by methodologies
11 described previously.

12 The use of other ethynyl containing reagents, such as
13 1-ethynyl-1-cyclohexanol and 1,
14 1'-ethynylendicyclohexanol, can be directly coupled, due to
15 the presence of hydroxyl (OH) bonds, to either halosilane
16 (Si-X, where X= F, Cl, Br) and/or silanol (Si-OH) groups in
17 the pre-ceramic polymer.

18 The use of benzoyl peroxide or other chemical catalysts

1 in conjunction with double or triple bonded carbon side
2 groups within the pre-ceramic polymer to achieve
3 crosslinking.

4 A single-step fabrication process of continuous ceramic
5 fiber ceramic matrix composites employs a thermoplastic
6 photo-curable pre-ceramic polymer in which the component is
7 shaped by a variety of standard composite fabrication
8 techniques, such as filament winding, tape winding, and
9 woven cloth winding. The process includes steps of passing
10 ceramic fiber monofilament, tow, mat, or woven cloth through
11 a solution of the thermoplastic photo-curable pre-ceramic
12 polymer, applying ceramic fiber monofilament, tow, mat, or
13 woven cloth to a moving flat substrate and using a heated or
14 unheated compaction roller to press the thermoplastic pre-
15 ceramic polymer coated ceramic fiber onto flat substrate.
16 The process also includes the steps of using photo-light of
17 the ultraviolet, visible, or infrared light spectrum to
18 induce cross-linking (curing) of the photo-curable pre-

1 ceramic polymer thereby rendering a thermoset polymer and
2 either partially or completely pyrolyzing the now cured pre-
3 ceramic polymer matrix coated ceramic fiber material. The
4 pre-ceramic polymer poly(ethynyl)carbosilane yields silicon
5 carbide upon pyrolysis. The pre-ceramic polymer may also
6 yield oxide ceramic such as aluminum oxide upon pyrolysis.
7 Other photo-curable pre-ceramic polymers may yield silicon
8 nitride, aluminum nitride and titanium carbide, for example.

9 A process of forming a photo-curable pre-ceramic
10 polymer, poly(ethynyl)-carbosilane to silicon carbide
11 ceramic includes the steps of reacting sodium acetylide
12 with organo-chlorosilanes and condensing (polymerizing) the
13 resultant organo-(ethynyl)chlorosilane product of step a
14 with an excess of an alkali metal. The organochlorosilane
15 is selected from a group of one or more of the following:
16 dichlorodimethylsilane, trichloro-phenylsilane (tri-
17 functional), and methyltrichlor.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)-carbosilane to silicon carbide
2 ceramic includes the steps of reacting sodium acetylide
3 with organochloro-silanes and condensing (polymerizing) the
4 resultant organo(ethynyl)-chlorosilane product of step a
5 with an excess of an alkali metal sodium.

6 A process of forming a photo-curable pre-ceramic
7 polymer, poly(ethynyl)-carbosilane, to silicon carbide
8 ceramic includes the steps of reacting sodium acetylide with
9 a mixture of organodichlorosilanes and organo-
10 trichlorosilanes and condensing (polymerizing) the
11 resultant organo(ethynyl)-chlorosilane product of step a
12 with an excess of an alkali metal.

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-carbosilane to silicon carbide
15 ceramic includes the steps of reacting a sub-stoichiometric
16 amount of an alkali metal with organochloro-silanes and
17 reacting the partially polymerized polyorganochlorosilane
18 with sodium acetylide. The organochlorosilane is selected

1 from a group consisting of one or more of the following:
2 dichlorodimethylsilane, trichlorophenylsilane (tri-
3 functional) and methyltrichlorosilane.

4 A process of forming a photo-curable pre-ceramic
5 polymer, poly(ethynyl)-carbosilane to silicon carbide
6 ceramic includes the steps of reacting a sub-
7 stoichiometric amount of sodium metal with
8 organochlorosilanes and reacting the partially polymerized
9 polyorganochlorosilane with sodium acetylide.

10 A process of forming a photo-curable pre-ceramic
11 polymer, poly(ethynyl)carbosilane to silicon carbide
12 ceramic includes the steps of reacting a sub-stoichiometric
13 amount of an alkali metal with a mixture of organodichloro-
14 silanes and organotrichlorosilanes and reacting the
15 partially polymerized polyorganochlorosilane with sodium
16 acetylide.

17 A process of forming a photo-curable pre-ceramic
18 polymer, poly(ethynyl)silazane, to silicon nitride ceramic

1 includes the steps of reacting sodium acetylide with
2 organochlorosilanes and condensing (polymerizing) the
3 resultant organo(ethynyl)chlorosilane product of step a with
4 ammonia.

5 A process of forming a photo-curable pre-ceramic
6 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
7 includes the steps of reacting sodium acetylide with
8 organochlorosilanes and condensing (polymerizing) the
9 resultant organo(ethynyl)-chlorosilane product of step a
10 with ammonia.

11 A process of forming a photo-curable pre-ceramic
12 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
13 includes the steps of reacting sodium acetylide with a
14 mixture of organodichlorosilanes and organotrichloro-silanes
15 and condensing (polymerizing) the resultant organo(ethynyl)-
16 chlorosilane product of step a with ammonia. The
17 organochlorosilane is selected from a group consisting of
18 one or more of the following: dichlorodimethylsilane,

1 trichlorophenylsilane (tri-functional) and methyltrichloro-
2 silane.

3 A process of forming a photo-curable pre-ceramic
4 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
5 includes the steps of reacting a sub-stoichiometric amount
6 of ammonia with organochlorosilanes and reacting the
7 partially polymerized polyorganochlorosilazane with sodium
8 acetylide.

9 A process of forming a photo-curable pre-ceramic
10 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
11 includes the steps of reacting a sub-stoichiometric amount
12 of ammonia with organochlorosilanes and reacting the
13 partially polymerized polyorganochlorosilazane with sodium
14 acetylide.

15 A process of forming a photo- curable pre-ceramic
16 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
17 includes the steps of reacting a sub-stoichiometric amount
18 of ammonia with with a mixture of organodichloro-silanes and

1 organotrichlorosilanes and reacting the partially
2 polymerized polyorganochlorosilazane with sodium acetylide.

3 A process for fabricating a ceramic matrix composites
4 includes the steps of preparing a solution of thermoplastic
5 photo-curable pre-ceramic polymer, passing a pre-preg
6 through the solution of thermoplastic photo-curable pre-
7 ceramic polymer, applying the pre-preg to a shaped mandrel,
8 using light energy to induce cross-linking of the
9 photo-curable pre-ceramic polymer after application to the
10 mandrel whereby the thermoplastic pre-ceramic polymer is
11 curved and pyrolyzing the cured thermoplastic pre-ceramic
12 polymer matrix composite material.

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-carbosilane to silicon carbide
15 ceramic includes the steps of (a) reacting sodium acetylide
16 with organo-chlorosilanes and (b) condensing (polymerizing)
17 the resultant organo-(ethynyl)chlorosilane product of step a
18 with an excess of an alkali metal. The organochlorosilane

1 is selected from a group of one or more of the following:
2 dichlorodimethylsilane, trichloro-phenylsilane (tri-
3 functional) and methyltrichlorosilane.

4 A process of forming a photo-curable pre-ceramic
5 polymer, poly(ethynyl)-carbosilane to silicon carbide
6 ceramic includes the steps of (a) reacting sodium acetylide
7 with organochloro-silanes and (b) condensing (polymerizing)
8 the resultant organo(ethynyl)-chlorosilane product of step a
9 with an excess of an alkali metal sodium. The rganochloro-
10 silane is selected from a group consisiting of one or more
11 of the following: dichlorodimethylsilane, trichlorophenyl-
12 silane (tri-functional) and methyltrichlorosilane.

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)-carbosilane, to silicon carbide
15 ceramic includes the steps of (a) reacting sodium acetylide
16 with a mixture of organodichlorosilanes and organotrichloro-
17 silanes and (b) condensing (polymerizing) the resultant
18 organo(ethynyl)-chlorosilane product of step a with an

1 excess of an alkali metal.

2 A process of forming a photo-curable pre-ceramic
3 polymer, poly(ethynyl)-carbosilane to silicon carbide
4 ceramic includes the steps of (a) reacting a sub-
5 stoichiometric amount of an alkali metal with organochloro-
6 silanes and (b) reacting the partially polymerized
7 polyorganochlorosilane with sodium acetylide. The
8 organochlorosilane is selected from a group consisting of
9 one or more of the following: dichlorodimethylsilane,
10 trichlorophenylsilane (tri-functional) and
11 methyltrichlorosilane.

12 A process of forming a photo-curable pre-ceramic
13 polymer, poly(ethynyl)- carbosilane to silicon carbide
14 ceramic includes the steps of reacting a sub-stoichiometric
15 amount of sodium metal with organochloro- silanes and
16 reacting the partially polymerized polyorganochlorosilane
17 with sodium acetylide. The organochlorosilane is selected
18 from a group consisting of one or more of the following:

1 dichlorodimethylsilane, trichlorophenylsilane (tri-
2 functional) and methyltrichloro- silane.

3 A process of forming a photo-curable pre-ceramic
4 polymer, poly(ethynyl)carbosilane to silicon carbide ceramic
5 includes the steps of reacting a sub-stoichiometric amount
6 of an alkali metal with a mixture of organodichloro- silanes
7 and organotrichlorosilanes and reacting the partially
8 polymerized polyorganochlorosilane with sodium acetylide.

9 A process of forming a photo-curable pre-ceramic
10 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
11 includes the steps of reacting sodium acetylide with
12 organochlorosilanes and condensing (polymerizing) the
13 resultant organo(ethynyl)chloro-silane product of step a
14 with ammonia. The organochlorosilane is selected from a
15 group consisting of one or more of the following:
16 dichlorodimethylsilane, trichlorophenylsilane (tri-
17 functional) and methyltrichlorosilane.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
2 includes the steps of reacting sodium acetylide with
3 organochlorosilanes and condensing (polymerizing) the
4 resultant organo(ethynyl) chloro-silane product of step a
5 with ammonia. The organochlorosilane is selected from a
6 group consisting of one or more of the following:
7 dichlorodimethylsilane, trichlorophenylsilane (tri-
8 functional) and methyltrichlorosilane.

9 A process of forming a photo-curable pre-ceramic
10 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
11 includes the steps of reacting sodium acetylide with a
12 mixture of organodichlorosilanes and organotrichlorosilanes
13 and condensing (polymerizing) the resultant organo-
14 (ethynyl)chloro-silane product of step a with ammonia.

15 A process of forming a photo-curable pre-ceramic
16 polymer, poly(ethynyl)silazane to silicon nitride ceramic
17 includes the steps of reacting a sub-stoichiometric amount
18 of ammonia with organo-chlorosilanes and reacting the

1 partially polymerized polyorganochlorosilazane with sodium
2 acetylide. The organochlorosilane is selected from a group
3 consisting of one or more of the following: dichlorodi-
4 methylsilane, trichlorophenylsilane (tri-functional) and
5 methyltrichlorosilane.

6 A process of forming a photo-curable pre-ceramic
7 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
8 includes the steps of reacting a sub-stoichiometric amount
9 of ammonia with organochlorosilanes and reacting the
10 partially polymerized polyorganochlorosilazane with sodium
11 acetylide. The organochlorosilane is selected from a group
12 consisting of one or more of the following: dichlorodi-
13 methylsilane, trichlorophenylsilane (tri-functional) and
14 methyltrichlorosilane.

15 A process of forming a photo- curable pre-ceramic
16 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
17 includes the steps of reacting a sub-stoichiometric amount
18 of ammonia with a mixture of organodichlorosilanes and

1 organotrichlorosilanes and reacting the partially
2 polymerized polyorganochlorosilazane with sodium acetylide.

3 A process for fabricating a ceramic matrix composites
4 includes the steps of preparing a solution of thermoplastic
5 photo-curable pre-ceramic polymer, passing a pre-preg
6 through the solution of thermoplastic photo-curable pre-
7 ceramic polymer, applying the pre-preg to a shaped mandrel,
8 using light energy to induce cross- linking of the
9 photo-curable pre-ceramic polymer after application to the
10 mandrel whereby the thermoplastic pre-ceramic polymer is
11 curved and pyrolyzing the cured thermoplastic pre-ceramic
12 polymer matrix composite material.

13 A single-step fabrication of continuous ceramic fiber
14 ceramic matrix composites employing a thermoplastic
15 photo-curable pre-ceramic polymer in which the component is
16 shape by a variety of standard composite fabrication
17 techniques, such as filament winding, tape winding, and
18 woven cloth winding includes steps of passing ceramic fiber

1 monofilament, tow, mat, or woven cloth through a solution of
2 the thermoplastic photo-curable pre-ceramic polymer,
3 applying ceramic fiber monofilament, tow, mat, or woven
4 cloth to a shaped mandrel, using photo-energy of the
5 ultraviolet, visible or infrared light spectrum to induce
6 cross-linking (curing) of the photo-curable pre-ceramic
7 polymer after application to the mandrel and either
8 partially or completely pyrolyzing the now cured pre-ceramic
9 polymer matrix composite material. The pre-ceramic polymer
10 is poly(ethynyl)carbosilane. The pre-ceramic polymer may
11 yield silicon carbide upon pyrolysis. The pre-ceramic
12 polymer may yield an oxide ceramic upon pyrolysis. The pre-
13 ceramic polymer may yield titanium carbide upon pyrolysis.
14 The pre-ceramic polymer may yield aluminum nitride upon
15 pyrolysis. The pre-ceramic polymer may yield silicon
16 nitride upon pyrolysis. The pre-ceramic polymer may yield
17 aluminum oxide upon pyrolysis.

18 A single-step fabrication of continuous ceramic fiber

1 ceramic matrix composites employing a thermoplastic photo-
2 curable pre-ceramic polymer in which the component is shape
3 by a variety of standard composite fabrication techniques,
4 such as filament winding, tape winding, and woven cloth
5 winding under inert atmosphere includes steps of passing
6 ceramic fiber monofilament, tow, mat, or woven cloth through
7 a solution of the thermoplastic photo-curable pre-ceramic
8 polymer, applying ceramic fiber monofilament, tow, mat, or
9 woven cloth to a shaped rotating mandrel, use of a heated or
10 unheated compaction roller to press the thermoplastic pre-
11 ceramic polymer onto the mandrel, using ultraviolet,
12 visible, or infrared light to induce cross-linking (curing)
13 of the photo-curable pre-ceramic polymer thereby rendering a
14 thermoset polymer, either partially or completely pyrolyzing
15 the now cured pre-ceramic polymer matrix material and
16 followed by the final heat treatment of the shaped ceramic
17 matrix composite "brown body". The pre-ceramic polymer is
18 poly(ethynyl)carbo- silane. The pre-ceramic polymer may

1 yield silicon carbide upon pyrolysis. The pre-ceramic
2 polymer may yield an oxide ceramic upon pyrolysis. The pre-
3 ceramic polymer may yield titanium carbide upon pyrolysis.
4 The pre-ceramic polymer may yield aluminum nitride upon
5 pyrolysis. The pre-ceramic polymer may yield silicon
6 nitride upon pyrolysis. The pre-ceramic polymer may yield
7 aluminum oxide upon pyrolysis.

8 A single-step fabrication of continuous ceramic fiber
9 ceramic matrix composites employing a thermoplastic
10 photo-curable pre-ceramic polymer in which the component is
11 shape by a variety of standard composite fabrication
12 techniques, such as filament winding, tape winding, and
13 woven cloth winding, includes steps of passing ceramic fiber
14 monofilament, tow, mat, or woven cloth through a solution of
15 the thermoplastic photo-curable pre-ceramic polymer,
16 applying ceramic fiber monofilament, tow, mat, or woven
17 cloth to a moving flat substrate, using a compaction roller
18 to press the thermoplastic pre-ceramic polymer coated

1 ceramic fiber onto flat substrate, using photo-light of the
2 ultraviolet, visible, or infrared light spectrum to induce
3 cross-linking (curing) of the photo-curable pre-ceramic
4 polymer thereby rendering a thermoset polymer and either
5 partially or completely pyrolyzing the now cured pre-ceramic
6 polymer matrix coated ceramic fiber material. The pre-
7 ceramic polymer is poly(ethynyl)carbosilane. The pre-
8 ceramic polymer may yield silicon carbide upon pyrolysis.
9 The pre-ceramic polymer may yield an oxide ceramic upon
10 pyrolysis. The pre-ceramic polymer may yield titanium
11 carbide upon pyrolysis. The pre-ceramic polymer may yield
12 aluminum nitride upon pyrolysis. The pre-ceramic polymer
13 may yield silicon nitride upon pyrolysis. The pre-ceramic
14 polymer may yield aluminum oxide upon pyrolysis.

15 Photocurable poly(ethynyl)carbosilane can be
16 synthesized directly from difunctional and trifunctional
17 chlorosilane reagents with the addition of sub-
18 stoichiometric amounts of sodium to form poly(chloro)

1 silanes, followed by the addition of excess sodium acetylide
2 to provide photocurable cross-linking sites.

3 Sodium metal suspension (40 % by weight) in oil was
4 weighed. The suspension was washed three times in xylene
5 and separated by centrifugation. The washed sodium was added
6 to 200 ml of xylene in the triple-neck reaction vessel. The
7 refluxed reaction vessel was heated under flowing argon to
8 100 degrees Centigrade. The mixture of methylene bromide,
9 dichlorodimethylsilane and trichlorophenylsilane was slowly
10 added using a burette. An exothermic reaction ensued and
11 the temperature of reaction vessel contents reached 133
12 degrees Centigrade and the mixture boiled vigorously under
13 reflux for approximately 30 minutes. The mixture was
14 stirred for an additional hour while cooling. The dark
15 purple/brown mixture containing precipitates was filtered
16 and a clear yellow filtrate was obtained.

17 The resulting poly(chloro)carbosilane polymer was
18 extracted from the filtrate by evaporation in a Rotovapor

1 apparatus. The resulting dark yellow viscous polymer was
2 dissolved in tetrahydrofuran. The appropriate amount of
3 sodium acetylide powder was dissolved in dimethyl formamide
4 and added slowly to the poly(chloro)carbo-silane polymer
5 solution and an exothermic reaction occurs and the color of
6 the polymer solution turned a deep orange. Reaction
7 byproducts were removed by filtration and the final
8 poly(ethynyl)carbosilane polymer was obtained.

9 Six different examples of PECS, with varying ethynyl
10 groups concentrations have been prepared as shown in Table
11 1. Ethynyl concentration was varied from 0 to 25 percent
12 (by mole).

13 In order to characterize the molecular weight and
14 molecular weight distributions of polymers synthesized and
15 utilized in this study, HPLC was utilized. A carefully
16 prepared calibration curve was measured using NIST traceable
17 molecular weight standards and measuring elution time. From
18 this calibration curve, we were able to estimate the peak

1 molecular weight of the PECS synthesized based upon the
2 chromatograms. In Table 2 below, several of our polymers
3 are compared with Dow Corning PCS. Our materials were
4 purposely prepared as viscous fluids for greater ease in
5 fabrication.

6 Table 2: Molecular Weights and HPLC Elution Times (peak) for
7 PECS Synthesized by MATECH and Compared with Dow Corning
8 PCS.

9	POLYMER	ELUTION TIME	MORPHOLOGY	MOLECULAR WEIGHT
10	Dow Corning PCS	14.468	Solid Flake	4400
11	PECS (0% ethynyl) A	16.598	Viscous Fluid	750
12	PECS (0% ethynyl) B	16.449	Viscous Fluid	700
13	PECS (5% ethynyl)	16.050	Viscous Fluid	1300
14	PECS (15% ethynyl)	16.862	Viscous Fluid	600
15	PECS (20% ethynyl) A	16.504	Viscous Fluid	700
16	PECS (20% ethynyl) B	15.973	Viscous Fluid	1400
17	PECS (25 % ethynyl)	16.732	Viscous Fluid	580
18	Fabricate Coupon of Ceramic Fabric using PECS Polymer.			

1 One of the polymers synthesized as described above was
2 used to fabricate a ceramic matrix composite using woven
3 ceramic fabric. 7.0 grams of Poly(ethynyl)carbosilane with
4 15% ethynyl side-groups for cross-linking was impregnated
5 into 4 layers of woven ALTEX fabric. The resulting pre-preg
6 was photocured over night to produce cross-linked matrix and
7 then fired in Argon gas to 1200 degrees centigrade for one
8 hour. The resulting product was a ceramic coupon suitable
9 for testing and evaluation.

10 The polymer synthesized above, 7.0 grams of Poly
11 (ethynyl)carbosilane with 15% ethynyl side-groups for cross-
12 linking was impregnated into 4 layers of woven ALTEX fabric.
13 The resulting pre-preg was photocured over night to produce
14 cross-linked matrix and then fired in Argon gas to 1200
15 degrees centigrade for one hour. The resulting product was
16 a ceramic coupon suitable for testing and evaluation.

17 The resulting SiC ceramic matrix composite (CMC) has
18 been characterized. After only two processing cycles, the

1 resulting CMC has an apparent density of 2.134 grams/cc and
2 a porosity of 38.24 percent (%). In addition, it exhibits
3 good strength and sounds very much like a ceramic when
4 tapped. Scanning Electron Microscopy (SEM) photomicrographs
5 reveal that the woven fiber tows (of approximately 500
6 monofilaments each) are well bonded with minimal porosity,
7 even at high magnification. Large pores are still present
8 between tows, however, which can permit further
9 densification through repeated polymer-impregnation-
10 pyrolysis (PIP) cycles.

11 EXAMPLE 10

12 For 25% ethynyl side-group substitution, 11.50 grams of
13 sodium metal suspension (40 % sodium by weight) in oil was
14 weighed. The suspension was washed three times in xylene and
15 separated by centrifugation. The washed sodium was added to
16 200 ml of xylene in the triple-neck reaction vessel. The
17 refluxed reaction vessel was heated under flowing argon to
18 100 degrees centigrade. A mixture of 8.693 grams methylene

1 bromide, 4.840 grams dichlorodimethylsilane, and 1.869 grams
2 trichlorophenylsilane was slowly added using a burette. An
3 exothermic reaction ensued and the temperature of reaction
4 vessel contents reached 133 degrees centigrade and the
5 mixture boiled vigorously under reflux for approximately 30
6 minutes. The mixture was stirred for an additional hour
7 while cooling. The dark purple/brown mixture, containing
8 precipitates, was filtered and a clear yellow filtrate was
9 obtained.

10 The resulting poly(chloro)carbosilane polymer was
11 extracted from the filtrate by evaporation in a Rotovapor
12 apparatus. The resulting dark yellow viscous polymer was
13 dissolved in 50 ml tetrahydrofuran (THF). 0.600 grams of
14 sodium acetylide powder was dissolved in 5.0 ml dimethyl
15 formamide (DMF) and added slowly to the poly(chloro)carbo-
16 silane polymer solution and an exothermic reaction occurred
17 and the color of the polymer solution turned a deep purple-
18 red. Reaction byproducts were removed by filtration and the

1 final poly(ethynyl)carbosilane polymer dissolved in THF was
2 obtained. The polymer was then extracted from the filtrate
3 by evaporation in a Rotovapor apparatus, yielding
4 approximately 8.0 grams of poly(ethynyl)carbosilane.

5 EXAMPLE 11

6 For 20% ethynyl side-group substitution, 11.50 grams of
7 sodium metal suspension (40 % sodium by weight) in oil was
8 weighed. The suspension was washed three times in xylene and
9 separated by centrifugation. The washed sodium was added to
10 200 ml of xylene in the triple-neck reaction vessel. The
11 refluxed reaction vessel was heated under flowing argon to
12 100oC. A mixture of 8.693 grams methylene bromide, 5.163
13 grams dichlorodimethylsilane, and 1.495 grams
14 trichlorophenylsilane was slowly added using a burette. An
15 exothermic reaction ensued and the temperature of reaction
16 vessel contents reached 133 degrees centigrade and the
17 mixture boiled vigorously under reflux for approximately 30
18 minutes. The mixture was stirred for an additional hour

1 while cooling. The dark purple/brown mixture, containing
2 precipitates, was filtered and a clear yellow filtrate was
3 obtained.

4 The resulting poly(chloro)carbosilane polymer was
5 extracted from the filtrate by evaporation in a Rotovapor
6 apparatus. The resulting dark yellow viscous polymer was
7 dissolved in 50 ml tetrahydrofuran (THF). 0.480 grams of
8 sodium acetylide powder was dissolved in 5.0 ml dimethyl
9 formamide (DMF) and added slowly to the poly(chloro)-
10 carbosilane polymer solution and an exothermic reaction
11 occurred and the color of the polymer solution turned a deep
12 purple-red. Reaction byproducts were removed by filtration
13 and the final poly(ethynyl)carbosilane polymer dissolved in
14 THF was obtained. The polymer was then extracted from the
15 filtrate by evaporation in a Rotovapor apparatus, yielding
16 approximately 8.0 grams of poly(ethynyl)carbosilane.

17 EXAMPLE 12

18 For 15% ethynyl side-group substitution, 11.50 grams of

1 sodium metal suspension (40 % sodium by weight) in oil was
2 weighed. The suspension was washed three times in xylene
3 and separated by centrifugation. The washed sodium was
4 added to 200 ml of xylene in the triple-neck reaction
5 vessel. The refluxed reaction vessel was heated under
6 flowing argon to 100 degrees centigrade. A mixture of 8.693
7 grams methylene bromide, 5.485 grams dichlorodimethylsilane,
8 and 1.121 grams trichloro- phenylsilane was slowly added
9 using a burette. An exothermic reaction ensued and the
10 temperature of reaction vessel contents reached 133 degrees
11 centigrade and the mixture boiled vigorously under reflux
12 for approximately 30 minutes. The mixture was stirred for
13 an additional hour while cooling. The dark purple/brown
14 mixture, containing precipitates, was filtered and a clear
15 yellow filtrate was obtained.

16 The resulting poly(chloro)carbosilane polymer was
17 extracted from the filtrate by evaporation in a Rotovapor
18 apparatus. The resulting dark yellow viscous polymer was

1 dissolved in 50 ml tetrahydrofuran (THF). 0.360 grams of
2 sodium acetylide powder was dissolved in 5.0 ml dimethyl
3 formamide (DMF) and added slowly to the poly(chloro)carbo-
4 silane polymer solution and an exothermic reaction occurred
5 and the color of the polymer solution turned a deep purple-
6 red. Reaction byproducts were removed by filtration and the
7 final poly(ethynyl)carbosilane polymer dissolved in THF was
8 obtained. The polymer was then extracted from the filtrate
9 by evaporation in a Rotovapor apparatus, yielding
10 approximately 8.0 grams of poly(ethynyl)carbosilane.

11 EXAMPLE 13

12 For 10% ethynyl side-group substitution, 11.50 grams of
13 sodium metal suspension (40 % sodium by weight) in oil was
14 weighed. The suspension was washed three times in xylene
15 and separated by centrifugation. The washed sodium was added
16 to 200 ml of xylene in the triple-neck reaction vessel. The
17 refluxed reaction vessel was heated under flowing argon to
18 100°C. A mixture of 8.693 grams methylene bromide, 5.808

1 grams dichlorodimethylsilane, and 0.747 grams trichloro-
2 phenylsilane was slowly added using a burette. An
3 exothermic reaction ensued and the temperature of reaction
4 vessel contents reached 133 degrees centigrade and the
5 mixture boiled vigorously under reflux for approximately 30
6 minutes. The mixture was stirred for an additional hour
7 while cooling. The dark purple/brown mixture, containing
8 precipitates, was filtered and a clear yellow filtrate was
9 obtained.

10 The resulting poly(chloro)carbosilane polymer was
11 extracted from the filtrate by evaporation in a Rotovapor
12 apparatus. The resulting dark yellow viscous polymer was
13 dissolved in 50 ml tetrahydrofuran (THF). 0.240 grams of
14 sodium acetylide powder was dissolved in 5.0 ml dimethyl
15 formamide (DMF) and added slowly to the poly(chloro)-
16 carbosilane polymer solution and an exothermic reaction
17 occurred and the color of the polymer solution turned a deep
18 purple-red. Reaction byproducts were removed by filtration

1 and the final poly(ethynyl)carbosilane polymer dissolved in
2 THF was obtained. The polymer was then extracted from the
3 filtrate by evaporation in a Rotovapor apparatus, yielding
4 approximately 8.0 grams of poly(ethynyl)carbosilane.

5 EXAMPLE 14

6 For 5% ethynyl side-group substitution, 11.50 grams of
7 sodium metal suspension (40 % sodium by weight) in oil was
8 weighed. The suspension was washed three times in xylene
9 and separated by centrifugation. The washed sodium was added
10 to 200 ml of xylene in the triple-neck reaction vessel. The
11 refluxed reaction vessel was heated under flowing argon to
12 100 degrees centigrade. A mixture of 8.693 grams methylene
13 bromide, 6.131 grams dichlorodimethylsilane, and 0.374 grams
14 trichloro-phenylsilane was slowly added using a burette. An
15 exothermic reaction ensued and the temperature of reaction
16 vessel contents reached 133 degrees centigrade and the
17 mixture boiled vigorously under reflux for approximately 30
18 minutes. The mixture was stirred for an additional hour

1 while cooling. The dark purple/brown mixture, containing
2 precipitates, was filtered and a clear yellow filtrate was
3 obtained.

4 The resulting poly(chloro)carbosilane polymer was
5 extracted from the filtrate by evaporation in a Rotovapor
6 apparatus. The resulting dark yellow viscous polymer was
7 dissolved in 50 ml tetrahydrofuran (THF). 0.120 grams of
8 sodium acetylide powder was dissolved in 5.0 ml dimethyl
9 formamide (DMF) and added slowly to the poly(chloro)-
10 carbosilane polymer solution and an exothermic reaction
11 occurred and the color of the polymer solution turned a deep
12 purple-red. Reaction byproducts were removed by filtration
13 and the final poly(ethynyl)carbosilane polymer dissolved in
14 THF was obtained. The polymer was then extracted from the
15 filtrate by evaporation in a Rotovapor apparatus, yielding
16 approximately 8.0 grams of poly(ethynyl)carbosilane.

17 EXAMPLE 15

18 For 0% ethynyl side-group substitution, 11.50 grams of

1 sodium metal suspension (40 % sodium by weight) in oil was
2 weighed. The suspension was washed three times in xylene
3 and separated by centrifugation. The washed sodium was
4 added to 200 ml of xylene in the triple-neck reaction
5 vessel. The refluxed reaction vessel was heated under
6 flowing argon to 100°C. A mixture of 8.693 grams methylene
7 bromide, 6.454 grams dichlorodimethylsilane was slowly added
8 using a burette. An exothermic reaction ensued and the
9 temperature of reaction vessel contents reached 133 degrees
10 centigrade and the mixture boiled vigorously under reflux
11 for approximately 30 minutes. The mixture was stirred for
12 an additional hour while cooling. The dark purple/brown
13 mixture, containing precipitates, was filtered and a clear
14 yellow filtrate was obtained.

15 The resulting polycarbosilane polymer was extracted
16 from the filtrate by evaporation in a Rotovapor apparatus
17 yielding approximately 8.0 grams of polycarbosilane with no
18 ethynyl side-groups.

1 It has been demonstrated that several commercially
2 available preceramic polymers can be made photocurable. The
3 preceramic polymer CERASETTM SZ inorganic polymer sold by
4 Honeywell Advanced Composites, Inc., which is a silazane-
5 based polymer, can be made photocurable to both UV and blue
6 light through the addition of photoinitiators. Also, the
7 preceramic polymer allylhydridopolycarbosilane (AHPCS)
8 polymer manufactured by Starfire Systems, Inc. can be made
9 photocurable to both UV and blue light through the addition
10 of photoinitiators.

11 EXAMPLE 16

12 A UV light photocurable polysilazane was produced by
13 mixing 2.00 grams of CERASETTM SZ inorganic polymer with
14 0.50 grams of IRGACURE® 1800, manufactured by Ciba Specialty
15 Chemicals, dissolved in 0.50 ml tetrahydrofuran. The
16 resulting yellow fluid, upon exposure to a high intensity UV
17 lamp, became a stiff, rigid polymer within an hour. The
18 resulting cross-linked polymer maintained its shape upon

1 heating and pyrolysis to 1200 degrees centigrade in flowing
2 argon gas. The ceramic yield of the pyrolyzed polymer was
3 in excess of 80 percent. A control sample, without the
4 photoinitiator, remained fluid after in excess of 24 hours
5 of continuous UV irradiation.

6 EXAMPLE 17

7 A blue light photocurable polysilazane was produced by
8 mixing 2.00 grams of CERASETTM SZ inorganic polymer with
9 0.50 grams of Camphorquinone, obtained from Aldrich Chemical
10 Company, dissolved in 0.50 ml tetrahydrofuran. The resulting
11 yellow fluid, upon exposure to a high intensity blue lamp,
12 became a stiff, rigid polymer within an hour. The resulting
13 cross-linked polymer maintained its shape upon heating and
14 pyrolysis to 1200 degrees Centigrade in flowing argon gas.
15 The ceramic yield of the pyrolyzed polymer was in excess of
16 80 percent. A control sample, without the photoinitiator,
17 remained fluid after in excess of 24 hours of continuous
18 blue light irradiation.

1 EXAMPLE 18

2 A UV light photocurable allylhydridocarbosilane was
3 produced by mixing 2.00 grams of allylhydridocarbosilane
4 (15% allylchloride) polymer with 0.50 grams of IRGACURE®
5 1800, manufactured by Ciba Specialty Chemicals, dissolved in
6 0.50 ml tetrahydrofuran. The resulting yellow fluid, upon
7 exposure to a high intensity UV lamp, became a stiff, rigid
8 polymer within an hour. The resulting cross-linked polymer
9 maintained its shape upon heating and pyrolysis to 1200
10 degrees Centigrade in flowing argon gas. The ceramic yield
11 of the pyrolyzed polymer was in excess of 80 percent. A
12 control sample, without the photoinitiator, remained fluid
13 after in excess of 24 hours of continuous UV irradiation.

14 EXAMPLE 19

15 A blue light photocurable allylhydridocarbosilane was
16 produced by mixing 2.00 grams of allylhydridocarbosilane
17 (15% allylchloride) polymer with 0.50 grams of Camphor-
18 quinone, obtained from Aldrich Chemical Company, dissolved

1 in 0.50 ml tetrahydrofuran. The resulting yellow fluid,
2 upon exposure to a high intensity blue lamp, became a stiff,
3 rigid polymer within an hour. The resulting cross-linked
4 polymer maintained its shape upon heating and pyrolysis to
5 1200 degrees Centigrade in flowing argon gas. The ceramic
6 yield of the pyrolyzed polymer was in excess of 80 percent.
7 A control sample, without the photo-initiator, remained
8 fluid after in excess of 24 hours of continuous blue light
9 irradiation.

10 EXAMPLE 20:

11 10 g (31.2 mmol) HfCl_4 was put into 15 ml triethylamine,
12 forming a solid-liquid mixture. To this mixture 1.88 g
13 (31.2 mmol) ethylene-diamine was added drop wise over 5
14 minutes, while the mixture was stirred intensively. When
15 the addition was finished almost all of the liquid triethyl-
16 amine formed a solid hydrochloride salt. Excess
17 triethylamine removed by distillation and the remaining
18 solid powder heated up. It melted at around 140-160 degrees

1 centigrade. The temperature was increased up to 280 degrees
2 centigrade until it became a clear, transparent, highly
3 fluid polymer melt. After cooling to room temperature, it
4 solidified and was easy to break into small particles, so it
5 appeared like a powder. Solid polymer was melted completely
6 around 120-160 degrees centigrade and slowly cooled down to
7 temperature where the viscosity was high enough to pull
8 fiber. That temperature was around 110-120 degrees
9 centigrade when solid polymer started to melt at the time of
10 heating up. Fiber was pulled from the viscous melt.
11 Fiber kept in a closed glass tube under inert gas (nitrogen)
12 was exposed to UV light for 18 hours.

13 EXAMPLE 21:

14 The cross-linked fiber of EXAMPLE 20 was placed into an open
15 tube with N2 gas flowing through and heated up to 1100
16 degrees centigrade with a very low heating speed of around 1
17 degrees per minute. The resulting fiber after firing was a
18 black HfC containing ceramic fiber that also contains some

1 nitrogen.

2 EXAMPLE 22:

3 The cross-linked fiber of EXAMPLE 20 was placed into an open
4 tube with NH₃ gas flowing through and heated up to 1100
5 degrees centigrade with a very low heating speed, around 1
6 degrees per minute. As a result, after firing, a white HfN
7 fiber was observed.

8 EXAMPLE 23:

9 10 g (31.2 mmol) HfCl₄ was put into 15 ml triethylamine,
10 forming a solid-liquid mixture. To this mixture 0.94 g
11 (15.6 mmol) ethylene-diamine and 0.89 g (15.6 mmol)
12 allylamine were added drop wise, simultaneously over 5
13 minutes, while the mixture was stirred intensively. When
14 the addition was finished almost all of the liquid triethyl-
15 amine formed a solid hydrochloride salt. Excess triethyl-
16 amine removed by distillation and the remaining solid powder
17 heated up. It melted at around 80-100 degrees centigrade.
18 The temperature was increased up to 260 degrees centigrade

1 until it became a clear, transparent, highly fluid polymer
2 melt. After cooling to room temperature, it solidified and
3 was easy to break into small particles, so it appeared like
4 a powder. Solid polymer was melted completely around 100-
5 120 degrees centigrade and slowly cooled down to temperature
6 where the viscosity was high enough to pull fiber. That
7 temperature was around 70-80 degrees centigrade when solid
8 polymer started to melt at the time of heating up. Fiber was
9 pulled from the viscous melt. Fiber kept in a closed glass
10 tube under inert gas (nitrogen) was exposed to UV light for
11 18 hours.

12 EXAMPLE 24:

13 The cross-linked fiber of EXAMPLE 23 was placed into an open
14 tube with nitrogen gas flowing through and heated up to 1100
15 degrees centigrade with a very low heating speed of around 1
16 degree per minute. The resulting fiber after firing was a
17 black HfC containing ceramic fiber that also contains some
18 nitrogen.

1 EXAMPLE 25:

2 The cross-linked fiber of EXAMPLE 23 was placed into an open
3 tube with NH₃ gas flowing through and heated up to 1100
4 degrees centigrade with a very low heating speed, around 1
5 degree per minute. As a result, after firing, a white HfN
6 fiber was observed.

7 EXAMPLE 26.

8 10 g (31.2 mmol) HfCl₄ was added slowly into 10 g (113.6
9 mmol) N,N'-dimethyl-ethylene-diamine liquid at room
10 temperature, while the mixture was stirred intensively.
11 Intensive heat and purple color developed. When the addition
12 was finished temperature increased to 160 degrees
13 centigrade. After cooling to room temperature, it
14 solidified and was easy to break into small particles, so it
15 appeared like a purple powder. Solid was placed into a
16 round shape flask, put on a rotavapor under motor vacuum and
17 the temperature was increased. A small amount of liquid
18 collected (excess of N,N'-dimethyl-ethylene-diamine),

1 however, the solid did not melt even up to 280 degrees
2 centigrade. It was not used for fiber pulling.

3 EXAMPLE 27.

4 To 5 g (56.8 mmol) N,N'-dimethyl-ethylenediamine 12 g (37.5
5 mmol) hafnium-chloride was added slowly. Intensive heat and
6 purple color developed. To this liquid 1.92g (40 mmol)
7 sodium-acetylide was added as suspension in n-hexane.
8 Mixture of 1ml dimethylformamide (DMF) and 20ml
9 dichloromethane was added to the reaction mixture. Intensive
10 heat developed again and sodium chloride precipitated out
11 from the solution. After filtration, solvent was removed by
12 rotavapor and the remaining dark brown, viscous oil was
13 heated up to 200 degrees centigrade under motor vacuum. The
14 vacuum and heat-treated oil was cooled down to room
15 temperature. It solidified and was easy to break into small
16 particles, so it appeared like a dark brown powder. The
17 solid polymer was melted completely around 80-110 degrees
18 centigrade and slowly cooled down to temperature where the

1 viscosity was high enough to pull fiber. That temperature
 2 was around 90-100 degrees centigrade. Fiber was pulled from
 3 the viscous melt. The resulting fiber was photocured under
 4 ultraviolet light. After curing, the fiber was heat treated
 5 under flowing nitrogen gas to 1100 degrees centigrade.

6 Table 1: Selected Physical Constants of Hafnium Carbide,
 7 Nitride, and Oxide

8 Table 2: Summary of Results of Preliminary HfCN Preceramic
 9 Polymer Trials.

Name	Condition	polymer g	Melting point °C	Hf g/polymer g	Ceramic Yield	Hafnium yield
PEHN-1	1:1/CH ₂ Cl ₂	16.39	100-110	0.53	16.36%	29.62%
PEHN-1/1	1:1/CH ₂ Cl ₃ (two step)	14.96	N/A	0.58	20.37%	33.66%
PEHN-2	1:1/CH ₂ Br ₂	27	100-140	0.32	18.18%	54.22%
PEHN-3	1:1/CHCl ₃ +TEA	13.6	N/A	0.64	16.36%	24.58%

PEHN-4	1:1/No solvent	14	N/A	0.62	15.38%	23.79%
PEHN-5	1:1/Pyridine	13	N/A	0.67	26.00%	37.33%
PEHN-6	1:1.5 (Hf) /CH ₂ C 12	21.81	N/A	0.60	19.00%	30.51%
PEHN-7	0.5:1 (Hf) /CH ₂ B r2	16.1	N/A	0.54	26.40%	46.94%
PEI	1:1/CH ₂ Cl ₂	21.8	N/A	0.40	18.80%	45.26%
EDA	1:1/pyridine	37.2	150-200	0.23	16.80%	69.02%
Acetyli de	0.5/1Hf/acetyl ide	17	N/A	0.51	42.78%	80.31%

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7 From the foregoing it can be seen that processes of
8 forming a photo-curable pre-ceramic polymer and their
9 applications have been described.

10 Accordingly it is intended that the foregoing
11 disclosure shall be considered only as an illustration of
12 the principle of the present process.